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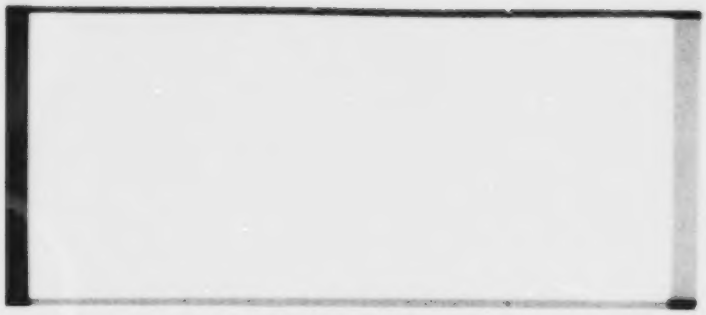

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FINAL REPORT

«CONVERSION OF SYNTHESIS GAS TO DISTILLATE OVER IRONBOROSILICATE ZEOLITES»

Dossier CRIQ no: 667-60133

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MICROMEDIA

PREFACE

This cost-shared project has been successfully completed with the help of the following participants:

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ABSTRACT

The work carried out within the framework of this project has focused mainly on the modification of a proprietary multi-functional crystalline ironborosilicate zeolite designated as ZKQ-IB4A for the purpose of maximising premium grade diesel production from synthesis gas. Following a brief review of the pertinent literature on the various metals employed in modifying the base zeolite, the methods used in incorporating such metals are fully described and the characterization results are presented and discussed.

Twelve catalysts prepared by modifying the ZKQ-IB4A base zeolite with Na, Co and La, Ru and Zn were each tested in a small fixed-bed tubular reactor for 366 hours in the majority of cases. The effect of preoxidising the catalyst and of the use of Sterotex as a lubricant for facilitating pelletisation of the catalyst on catalytic activity and selectivity is discussed.

Aside from showing the central role of sodium in controlling both the activity and the selectivity of the catalyst which are equally dependent on the method used in incorporating it in the catalyst, the results also point to the likely existence of an optimum Na concentration for maximising liquid hydrocarbons yield.

All the catalysts produced both gasoline and distillate range hydrocarbons which are mainly composed of straight chain paraffins. The gasoline to diesel ratio is, however, different for each catalyst. Co, Na-exchanged and La-impregnated base zeolite was found to be highly selective to diesel range hydrocarbons whereas Ru-impregnated base zeolite was found to actually decrease activity which was quite contrary to expectation on account of the fact that this metal has been shown by other workers to have the highest activity in F-T synthesis.

Further maximisation of diesel yield by oligomerising C_2 to C_7 olefins at high pressures over pentasil zeolites of low acidity is suggested.

Preoxidised sodium-containing base zeolite was found to be catalytically inactive and a subsequent reduction in flowing hydrogen/helium restored its activity.

Catalytic activity and selectivity were affected by Sterotex which was admixed with the catalyst prior to pelletisation.

Zn-exchanged and La-impregnated base zeolite displayed the highest liquid hydrocarbon selectivity but as to be expected, the product was high octane gasoline.

On the basis of the results obtained, the possibility of using modified ZKQ-IB4A catalysts in a process that could advantageously compete with the MOGD process (Mobil's Olefins to Gasoline and Distillate) is suggested.

Finally, recommendations are made in relation to future work aimed at the development of an integrated process that could control the gasoline to diesel ratio in order to meet shifts in demand. Towards this end, the need to find the optimum Na concentration that would maximise the yield of liquid hydrocarbons and the effect of such process variables as the H_2: CO ratios, temperature and pressure on catalytic activity and selectivity is stressed.

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RÉSUMÉ

Les travaux réalisés dans le cadre de ce projet ont porté principalement sur la modification d'une zéolithe synthétique à base de ferroborosilicate cristallin désignée comme ZKQ-IB4A dans le but de maximiser la production de diesel de bonne qualité à partir du gaz de synthèse.

Dans le présent rapport, on a donné un bref aperçu de la littérature touchant les divers métaux employés dans la modification du ZKQ-IB4A ainsi qu'une description détaillée des modes d'obtention des catalyseurs. On a également inclus une discussion des résultats de caractérisation des catalyseurs. Le restant du rapport est consacré à la présentation et à l'interprétation des résultats des tests ainsi qu'aux conclusions et recommandations d'usage qui s'imposent.

Chacun des douze catalyseurs préparés en modifiant la zéolithe de base avec Na, Co, La, Ru et Zn a été testé dans un petit réacteur tubulaire à lit fixe sur une durée de 366 heures dans la majorité des cas.

On a constaté que la préoxydation du catalyseur dans un courant d'oxygène et de l'emploi du sterotex comme lubrifiant pour faciliter la mise en forme du catalyseur influent sur l'activité et la sélectivité catalytiques.

Les résultats des tests ont permis non seulement de démontrer le rôle contrôleur du sodium sur l'activité et la sélectivité catalytiques, mais aussi la dépendance de celles-ci sur la façon dont le sodium est incorporé au catalyseur.

De plus, ces résultats nous portent à croire qu'il existe une concentration optimale de sodium qui conduirait à une maximisation du rendement en hydrocarbures liquides.

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De l'essence et du diesel à haute teneur en paraffines linéaires ont été obtenus de chacun des catalyseurs. Cependant, le rapport ratiométrique essence:diesel s'est avéré différent pour chacun des catalyseurs.

La zéolithe de base ayant subi un échange cationique successif avec du cobalt et du sodium suivi d'une imprégnation au lanthane a démontré une haute sélectivité vis-à-vis du diesel tandis que celle imprégnée au ruthénium a exibé une activité considérablement réduite contrairement aux attentes; selon d'autres chercheurs, le ruthénium possède la plus haute activité catalytique à l'égard de la synthèse F-T.

Le rendement en diesel pourrait être amélioré davantage en oligomérisant sous des pressions élevées les oléfines en C_2 à C_7 sur des zéolithes synthétiques pentasils à basse acidité.

La zéolithe de base préoxydée renfermant du sodium s'est avérée inactive mais une réduction subséquente dans un courant H_2/He a permis de restaurer son activité.

La plus haute sélectivité vis-à-vis des hycrocarbures liquides a été enregistrée avec la zéolithe de base ayant été préalablement soumise à un séchage cationique avec du zinc et à une imprégnation au lanthane. Comme on s'y attendait, le produit était constitué principalement par l'essence à haut indice d'octane.

À la lumière des résultats fort prometteurs à tous égards, on propose la poursuite des travaux en vue de développer un procédé utilisant les catalyseurs à base de ZKQ-IB4A, lequel pourrait concurrencer avantageusement avec le procédé MOGD (Mobil's Olefins to Gasoline and Distillate). Ce procédé permettrait de contrôler le rapport essence:diesel au besoin. Pour ce faire, il serait donc nécessaire de déterminer la concentration optimale du sodium qui permettrait la maximisation du rendement en hydro-

carbures liquides ainsi que les effets exercés par les conditions de travail comme le rapport H_2:CO, la température et la pression sur l'activité et la sélectivité catalytiques.

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1.0 INTRODUCTION

In recent years much emphasis has been placed on finding alternate sources of distillate fuels in view of the rapid depletion of high quality conventional paraffinic crudes and of the demand for diesel fuel which is expected to continue to rise throughout the 1990's. Tar sand derived bitumen has been touted as the major future source of diesel and jet fuels in Canada. Difficulties upgrading the middle and heavy cuts have so far not been totally surmounted on account of the mere fact that their compositions are vastly different from those of conventional crudes; so much so that some relaxation of product specifications is anticipated (1) and new catalysts which are more resistant to hetero-atom and heavy metal deactivation have to be developed. Improvement in the ignition properties of diesel fuel has been achieved through the use of cetane number boosters (2) with the attendant added costs. These boosters which are composed of organic nitrates such as octyl, amyl and hexyl nitrates have the disadvantage of producing upon combustion oxides of nitrogen which are highly undesirable atmospheric pollutants.

Alternate ways of producing high quality diesel fuel or a narrow specific range of straight chain paraffins that can be blended with poor quality distillate are being examined and foremost among which is the development of highly selective catalysts for the efficient conversion of synthesis gas into straight chain paraffins via the Fischer-Tropsch reaction (3) whose major limitation has heretofore been its lack of selectivity for a specific liquid fuel class. However, attempts have now been successfully made in circumventing the selectivity limitation imposed by the Anderson-Shulz-Flory distribution (4, 5) with the object of maximising the production of specific types of prod-

ucts such as gasoline (6-11), light olefins (12-14), heavy wax (15). Only methane and methanol can be produced with a 100% selectivity. In regard to the maximisation of synthetic diesel production with new or improved catalysts via the F-T reaction, however, there appears to be a paucity of information in the literature presumably because of overwhelming popularity of gasoline over diesel. In point of fact, much more emphasis has been placed on gasoline production.

As part of our continuing effort to contribute towards the development of highly catalysts for the production of synthetic transportation fuels, we have been able to develop a proprietary crystalline ironborosilicate pentasil zeolite designated as ZKQ-IB (11) which has demonstrated a high activity and selectivity in the production of gasoline via the F-T synthesis. In the introduction to our first report entitled «Direct Conversion of Synthesis Gas to High Octane Gasoline Over HZKQ-IB Zeolite» (16) to which the interested reader is advised to refer for detailed information on the catalysts used, mention was made of the MOGD process (Mobil Olefins to Gasoline and Distillate Process) (17), which has successfully passed the demonstration stage, as an alternate means of producing good quality diesel and jet fuels by oligomerising under moderate pressures (up to 10 Mpa) and at relatively low temperatures (200-250°C) olefins over ZSM-5 of low acidity. The olefins may come either from methanol or from the fluid catalytic cracking of conventional heavy oils. The distillate produced is highly olefinic and requires a subsequent mild hydrotreating prior to its use as premium grade diesel, aviation jet fuel or as a blending stock. By controlling process variables, the gasoline to diesel ratio can be adjusted from 0.9 to 0.1 in order to meet shifts in demand. When methanol is the primary feedstock, a first stage reactor packed with ZSM-5 operating at relatively high temperature (ca 600°C) and

under low pressures (1 bar) is required to convert it to olefins. The MOGD process thus constitutes the most recent advance in synthetic fuel production. In regard to this, our objective is to develop a process which could be controlled in such a way as to co-produce gasoline and diesel in the desired ratio via the F-T reaction thereby bypassing the methanol production and the methanol to olefins steps. It is noteworthy that according to the ASF distribution, the maximum selectivity to gasoline (C_5 -C_{11}) is around 47% where as that to diesel is about 52%. In the aforementioned report which dealt with the conversion of synthesis gas to high octane gasoline we reported the following major findings:

- It is entirely possible to convert synthesis gas selectively to high octane gasoline over a single particle catalyst comprising of an acidic crystalline ironborosilicate pentasil zeolite. The gasoline produced is highly olefinic and it has an aromatic content between 25 and 39 wt%. The higher the acidity of the zeolite the higher will be the aromatic content of the gasoline. No hydrocarbons with carbon number greater than C_{12} were produced.

- Improvement in the octane rating of the gasoline could be readily achieved by exchanging the H-form of the zeolite with nickel and zinc and calcining the exchanged zeolite at 500°C for several hours. The premium grade gasoline produced has an aromatic content of 50-60 wt%. Such a catalyst may perhaps be used in the production of certain aromatics from synthesis gas.

- By controlling the acidity of the catalyst through the use of alkaline metal ions such as those of sodium and potassium which neutralize the Bronsted acid sites, it is possible to co-produce a highly olefinic gasoline and a distillate comprising mainly of straight chain paraffins boiling mostly in the diesel range. Synthesis gas conversion decreases with increasing added amount of alkaline metal, which tends to shift the product distribution towards higher molecular weight products. C_{22} to C_{26} hydrocarbons are also formed albeit in very minor amounts. It appears that the presence of the zeolitic function tends to restrict chain growth beyond the diesel range.

- Modification of the base zeolite by cobalt exchange and impregnation with lanthanum significantly increases selectivity to liquid hydrocarbons at the expense of lighter ones. Production of organic oxygenates particularly alcohols appears to be enhanced in the presence of lanthanum.

In light of the foregoing, the present project must be viewed as a continuation of the first project in view of the fact that both projects involved the application of ZKQ-IB base catalysts to the direct conversion of synthesis gas to liquid transportation fuels.

As mentioned earlier the main objective of the present project was to find ways of modifying the ZKQ-IB base catalyst in order to maximise distillate fuel production at the expense of gasoline. In the course of the work a major preoccupation of ours has been to try to limit the excessive «loss» of carbon as CO_2 by lowering the rate of the shift reaction through the use of lower reaction temperature consistent with a reasonable syngas conversion and the addition of cobalt, which, when present on

the surface of the catalyst, is believed to suppress the internal shift reaction (14).

Briefly, modifications of the exhaustively prewashed base zeolite which had a very low residual sodium content were done via the following routes:

- Doping the base zeolite with sodium ions either by ion exchange followed by evaporation of the entire solution used for the exchange so that all of the added sodium ends up in the final composition of the catalyst or by direct impregnation using the wet incipient technique at room temperature. Doping was carried out at two sodium concentration levels namely 0.40 wt% and 0.67 wt% with respect to the weight of the base zeolite. At such concentrations, the Bronsted acid sites of the zeolite are expected to be neutralized on the basis of its acidity (1.61×10^{-4} moles NH_3/g) as determined by ammonia adsorption method (18) with katharometric means of detection. Cristalline borosilicate (19), iron silicate (20), titanoborosilicate (21) and ironborosilicate (11) pentasil zeolite are expected to have acidities lying between those of a crystalline aluminosilicate ZSM-5 zeolites with Si/Al ratios of 35 and 700 respectively. These two ZSM-5 zeolites have been shown to have acidities of 1.4 and 0.18 H^+/unit cell respectively, as measured by the pyridine adsorption method (22). Fe-ZSM-5 containing 5.0% Fe has an acidity of 0.25 H^+/unit cell.

- Ion exchange of the base zeolite with an aqueous solution of cobalt nitrate followed by refluxing the exchanged zeolite in an aqueous solution of sodium nitrate of the required concentration and evaporating to dryness. Thereafter, the oven-dried zeolite is impregnated with lanthanun nitrate solution by the wet incipient method. Ion exchange with cobalt was preferred over impregnation on the basis of an earliest study (16) which showed that Co-impregnated ZKQ-IB zeolite tended to favour methanation whereas the same zeolite which has been Co-exchanged did not show the same tendency but instead tended to favour the production of heavier hydrocarbons. The inclusion of cobalt in the base zeolite was based on the widespread knowledge that F-T synthesis on cobalt yields linear paraffins predominantly, part of which constitutes premium grade diesel. In point of fact, the first industrial production of transportation fuels via the F-T reaction was made possible by the use of a cobalt-based catalyst (5) having the following composition: 100 Co:5 ThO_2:8 MgO:200 kieselghur.

  Bifunctional catalysts comprising of cobalt as the active F-T metal and of a highly siliceous zeolite have been developed for the production of distillate fuels by workers of Union Carbide Corporation (23).

- Impregnation of the base zeolite with lanthanum with the object of maximising production of liquid hydrocarbons and reducing methanation and aromatisation, as has been shown in previous work (16); it is also common knowledge that La-exchanged X and Y zeolites are thermally highly stable and are therefore used in cracking processes.

- Impregnation of the base zeolite with ruthenium was carried out with the object of suppressing the shift reaction and of promoting the hydrogenation of olefins. Nearly half a century has elapsed since Pichler began studies of ruthenium catalysts that ultimately led to the synthesis of very high molecular weight polymethylene waxes (24). According to Vannice (25), who studied the F-T synthesis on transition metals supported on alumina, ruthenium was found to possess the highest activity. He showed that selectivity to C_{12+} hydrocarbons of Ru supported on silica was far much greater than that of Ru-Y zeolite (60% vs 1% w.r.t total hydrocarbons), indicating that chain growth was restricted by the zeolite pores.

Ruthenium catalysts are active over a wide range of temperatures (100-300°C) and pressures (1-2000 atmospheres). Depending on operating conditions and catalyst compositions, selectivity can vary from the sole production of methane to the production of polymethylene waxes. The latter is produced at low temperatures and high pressures, typically below 180°C and 1000 atmospheres (15).

Karn et al (26) studied the product distribution over 0.5% Ru on Al_2O_3 as a function of feed gas composition at 21.4 atmospheres. The major findings were that the molecular weight of the hydrocarbons decreased sharply as the CO content of the feed gas decreased and that the catalysts that make high molecular weight products must be selectively poisoned by CO.

King (27) studied Ru dispersed on various supports such as alumina, silica, silica-alumina, chroma-alumina, thoria, thoria-alumina, NaX and ultrastable zeolites. He found that catalysts supported on non-acidic NaY yielded substantial amounts of branched isomers whereas products from 2.5% Ru on silica showed substantial yields of straight-chain olefins and paraffins. Save for catalysts supported on silica-alumina and zeolites, all the other catalysts produced virtually no branched hydrocarbons. He also found that turnover numbers for CO and methane varied inversely with the degree of dispersion and that unsupported ruthenium produced the greatest amount of methane.

In another study conducted by Jacobs et al (28) on Ru-exchanged zeolites using $Ru(NH_3)_6^{3+}$ complex for the exchange, it was found that after reduction and chemisorption of H_2 and CO part of the Ru was in the sodalite cages and the rest in the supercages. With increasing reduction temperature in the range of 300-500°C there was a migration of the Ru in the sodalite cages to the supercages but there was no tendency for the Ru to aggregate into large cristallites or to move out of the pores.

Elliot and Lunsford (29) found that the addition of nickel to RuY wherein the Ru was deposited in the large cavities of the zeolite decreased the activity linearly whereas with the addition of copper the activity decreased sharply.

Selectivity to methane was found by Chen et al (30) to be strongly related to the zeolite type and the amount of residual sodium in the Ru-exchanged zeolite. The presence of alkaline ions appears to promote chain growth.

Huang and Haag (31) studied in detail synthesis gas conversion on Ru/ZSM-5 catalysts, with particular attention to the effects of various variables on activity and selectivity. These variables were: ruthenium loading, methods of catalyst preparations, type of zeolite, pressure, temperature, space velocity and H_2/CO ratio. The results showed that methane could be substantially reduced by higher pressure, lower space velocity, lower temperature and lower H_2/CO ratio; furthermore aromatics production would be greatly favoured by lower H_2/CO ratio at moderate temperature.

Kaliaguine et al (22) have found that Ru-ZSM-5 deactivates quite rapidly after showing very high activity at the beginning of the reaction. Methane selectivity was 17.7%, 59.5% and 86% at 250, 320 and 400°C respectively. This indirectly shows that with increasing temperature selectivity to C_{5+} hydrocarbons decreases.

The base catalyst used in this project is composed of a pentasil ironborosilicate zeolite which is intimately associated with oxides of iron. Excess iron is purposely added to the reaction mixture during synthesis and prior to hydrothermal crystallization. Some of the added iron ends up as framework iron while the remaining portion of the iron is transformed into iron oxides during calcination of the zeolite precursor.

The presence of iron oxides has been confirmed by XPS analysis (16). The zeolite and the iron oxides form such a homogeneous mixture that it is impossible to separate them by physical means. The iron oxides after pretreatment with hydrogen or synthesis gas become the active centre of F-T synthesis. One can liken these anchored oxides to precipitated supported F-T

iron catalysts in view of the fact that they are formed in hot alkaline medium.

Fe/zeolite catalysts have been studied by numerous workers for the production of gasoline (6, 9, 32-38). An excellent review of F-T iron catalysts is to be found in reference (39).

Methods of preparing metal/zeolite catalysts have until quite recently involved impregnation by the wet incipient technique (6, 33), physical blending (32), ion exchange (29) and precipitation of the metal on the zeolite. Except for the ion exchange method, these methods do not always lead to a uniform distribution or dispersion of the metal on the support. In F-T synthesis a high degree of dispersion is desirable in order to reduce aggregation of the metal into very large cristallites.

Relatively recent techniques of post-synthesis introduction of catalytically active metals onto or into porous supports such as zeolites, carbon molecular sieves and aerogels include the following:

- Immersion of the porous and activated zeolite (usually in the H-form) into a solution comprising of the metallo-organic compound of the required size and of an appropriate solvent, followed by sonication at room temperature. The solvent is then removed by evaporation and the resulting solid material is calcined in air at about 500°C for several hours. Metallo-organic compounds with sizes smaller than the pore opening of the zeolite can readily diffuse freely in the pores whereas those larger than the pore opening will not penetrate. Therefore, by selecting the compound with the right size and configuration one can thus deposit the metal inside or outside

the pore lattice as the case may be. Loss of the metallo-organic compound by evaporation or sublimation during calcination could be a serious drawback of this technique (40, 41).

- Gas phase adsorption of metallo-organic complexes which involves the slow heating of the complex and the zeolite in a tube sealed under vacuum at a temperature exceeding the sublimation or thermal degradation temperature of the complex. Following exposure to air at room temperature the resulting solid material is calcined in air at 550°C for several hours. Recovery of the metal in the catalyst appears to be high by this procedure.

- Atomisation of the metal of interest from a metal vapour generator directly on to the zeolite or more often than not in an organic solvent into which the zeolite is suspended. The metal atoms diffuse freely into the pores of the zeolite wherein it is highly dispersed upon removal of the solvent. This method of introducing highly dispersed metal on a support can only be carried out with dedicated special equipment.

Fischer-Tropsch synthesis on iron/zeolite of the ZSM-5 type catalysts has been investigated by various workers in an attempt to circumvent the selectivity limitation imposed by the Anderson-Shulz-Flory distribution function. In most cases the primary objective has been to achieve very high selectivity to gasoline or to the industrially important light olefins (6, 9, 32-38). An excellent review of F-T iron catalyst may be found in reference (39).

Inui et al (42) have employed a crystallization method which involves the dispersion of metal-loaded alumina powder in an aqueous solution containing sodium aluminate prior to gellation and the subsequent hydrothermal crystallization of the gel to zeolite wherein the metal is highly dispersed. This method has been shown to produce longer life catalysts which are less susceptible to coke formation. Similar preparative procedures were used by Sano et al (43) for the preparation of crystalline ironsilicate zeolite of the ZSM-5 type using finely ground magnetite powder as the source of iron.

As mentioned earlier the procedures used in the present work depart from those mentioned above in one major respect which is that aqueous solution containing excess iron is deliberately added to the reaction mixture during synthesis such that part of the iron ends up as framework iron whilst the remainder of the iron is highly dispersed on the zeolite.

All of the Fe/zeolite catalysts are at least bifunctional. The mode of action of such catalysts can best be described in terms of a «draining» effect exerted by the intense electrostatic field of the zeolite on the intermediates formed on the iron (32, 44). These intermediates are intercepted by the zeolite wherein they are converted into higher hydrocarbons with a maximum carbon number of 12 provided that the zeolite has Bronsted acid function. In the absence of such function, particularly when the acid sites are neutralized by alkaline metal ions, hydrocarbons with carbon numbers greater than 12 are formed. The mere presence of the zeolite appears to restrict in some measure the formation of wax.

Moreover, it is known that alkali metals such as Na and K tend to shift the product distribution to heavier products.

2.0 EXPERIMENTAL SECTION

In our previous report (16) a detailed account of the procedures used in the preparation of ZKQ-IB crystalline ironborosilicate zeolite was given. On the basis of the test results of several catalysts ZKQ-IB4A was selected for further study in this project on account of the fact that in the unmodified state diesel was co-produced with gasoline. The co-production of diesel was attributed to the presence of high residual sodium content occluded in the zeolite pore lattice which effectively neutralized part or all the Bronsted acid sites and most probably also in the iron oxide cristallites. The higher iron content of the catalyst could have played a certain role in promoting diesel formation particularly with the reduced aromatisation power of the catalyst.

The control of residual sodium content in the zeolite depends on how exhaustive is the washing of the zeolite, and whether hot or cold water is used for the washing. We have observed that ion exchange with ammonium ions at a temperature just below 100°C did not help in reducing the amount of residual sodium.

The method of introducing sodium in the catalyst is important because it influences above all the nature of the gaseous and liquid hydrocarbons. Doping with sodium was carried out by impregnation using the wet incipient method and by ion exchange followed by evaporation of the entire solution to dryness.

Modification of the base zeolite with several metals was carried out in an attempt to maximise the production of diesel at the expense of gasoline and to reduce excessive loss of carbon as CO_2 resulting from the shift reaction.

Hereinbelow is a detailed account of the procedures used in modifying ZKQ-IB4A base zeolite.

2.1 DESCRIPTION OF ZKQ-IB4A

ZKQ-IB is a crystalline ironborosilicate zeolite belonging to the pentasil family of zeolites. It may be represented empirically by the following formula expressed in terms of mole oxide ratios:

$$0.9\pm0.2M_{2/n}O:(aFe_2O_3:bB_2O_3):ySiO_2.zH_2O$$

wherein M is a cation of valence n such as that of the alkaline or alkaline earth metal. a and b are each greater than zero but less than 1 such that a + b = 1, y is equal to or greater than 4, and z is a number which can assume a value of 0 to 150 or more.

In practice M is sodium. Excess iron is purposely added to the reaction mixture during synthesis. Not all of the iron will be incorporated in the framework such that the iron lying without the framework acts as centres for F-T synthesis or participates in hydrocracking or cracking processes following sulfiding. It is noteworthy that the catalyst used in the CANMET hydrocracking process is an iron sulphide.

2.1.1 Preparation of ZKQ-IB4A

ZKQ-IB4A base zeolite was prepared in accordance with the procedures described in our previous technical report (16) in batches of about 200 ml. The mole oxide ratios of the various reagents used are given in Table 1.

TABLE 1: Mole oxide ratios of starting materials

CATALYSTS	$\frac{SiO}{B_2O_3}$	$\frac{SiO}{Fe_2O_3}$	$\frac{SiO}{(B_2O_3 + Fe_2O_3)}$	$\frac{OH}{SiO_2}$	$\frac{(TPA)_2O}{(TPA_2O + Na_2O)}$	$\frac{Na_2O}{(TPA)_2O}$	$\frac{TPA}{SiO_2}$	$\frac{H_2O}{OH}$	$\frac{H_2O}{SiO_2}$	pH
ZKQ-IB4A	8.40	15.41	5.43	0.5445	0.525	0.25	0.18	51.4	27.84	11.3

2.1.2 Modified catalysts

A) Sodium-impregnated ZKQ-IB4A (0.4 Na wt%) (Test no 2)

This catalyst was prepared by impregnating the HZKQ-IB4A base zeolite with an aqueous solution of sodium nitrate by the wet incipient method such that the final sodium content in the catalyst was 0.4 wt%. It was dried in a forced-air oven at 120°C for at least five hours and then calcined in air at 540°C for 10 hours using a heating rate of 3°C/minute. Thereafter the catalyst was allowed to cool to room temperature before it was pelletized without the use of a binder. 20 g of HZKQ-IB4A was used.

B) Co-exchanged and Na, La-impregnated catalyst (Test no 3) Co-ZKQ-IB4A (0.4 wt% Na+5 wt% La)

20 g of HZKQ-IB4A was exchanged with a 5% (w/v) aqueous solution of cobalt nitrate hexahydrate at about 90°C for 4 hours. The exchanged zeolite was separated by filtration using a Buchner funnel and Whatman 540 filter paper and washed copiously with deionized water until the filtrate gave a negative test for nitrate ions which involves the use of aqueous ferrous sulphate solution and concentrated sulphuric acid. After being dried at 120°C for at least five hours and then cooled to room temperature, the solid material was impregnated with an aqueous solu-

tion of sodium nitrate and lanthanum nitrate hexahydrate of the required strength to give a sodium and lanthanum content of 0.4 wt% and 5 wt% respectively. After drying at 100°C for 4 hours the material was calcined in air at 540°C for 10 hours to decompose the nitrates. Thereafter the catalyst was allowed to cool to room temperature before pelletization without the use of a binder.

C) Sodium-exchanged ZKQ-IB4A catalysts
ZKQ-IB4A-0.4 wt% Na (Test no 4)
and ZKQ-IB4A-0.67 wt% Na (Test no 5)

As mentioned earlier the product distributions from the Na-impregnated and Na-exchanged catalysts would most probably be different. Both catalysts were each prepared by exchanging HZKQ-IB4A with aqueous solutions of sodium nitrate of the appropriate strengths 90°C for 4 hours. Thereafter the entire solution was evaporated to dryness in each case over a heating plate and further dried in an oven at 120°C for 5 hours before being calcined in air at 540°C for 4 hours. The calcined material was then pelletized as such.

D) Cobalt, sodium-exchanged and lanthanum-impregnated catalysts
Co-ZKQ-IB4A-0.4 Na (La) (Test no 6)
and Co-ZKQ-IB4A-0.67 Na (La) (Test no 7)

Both catalysts were prepared by first exchanging HZKQ-IB4A with a 5% w/v aqueous cobalt nitrate solution at 90°C for 4 hours. Filtered, washed and dried at 120°C for at least 5 hours, the exchanged materials were each subjected to the same treatment as outlined in (c) for the incorporation of the required amount of sodium. Once dried at 120°C, the resulting solids were each impregnated with a solution of lanthanum to give a lanthanum

content of 5 wt% with respect to the catalyst in each case before being calcined at 540°C for 10 hours. The cooled catalysts were then pelletized as such.

E) Ruthenium-impregnated catalysts
ZKQ-IB4A (0.3 wt% Ru + 0.06 wt% Na) (Test no 10)
ZKQ-IB4A (0.5 wt% Ru + 0.27 wt% Na) (Test no 11)

20 g of HZKQ-IB4A was refluxed for two hours in 200 ml of an aqueous solution containing the required quantities of potassium ruthenate monohydrate. A 50 ml aqueous solution containing 0.05 g $NaNO_3$ or 0.2 g $NaNO_3$ as the case may be was then added and refluxing was continued for another hour. The whole mixture was then transferred quantitatively to a porcelaine evaporating dish and evaporated to dryness under an infrared lamp. The solid material was then calcined at 500°C for 3 hours and allowed to cool to room temperature before being pelletized.

G) Cobalt and sodium-exchanged and lanthanum-impregnated catalyst
Co, 0.67% Na-ZKQ-IB4A (5% La) (Test no 12)

The procedures employed were the same as in (d) except that the quantity of HZKQ-IB4A base zeolite used was 200 g instead of 20 g. This catalyst in pelletized form was subsequently sent to Professor B. Wojciechowski for testing.

H) Zinc-exchanged and lanthanum-impregnated catalyst Zn-ZKQ-IB4A (5% La) (Test no 13)

50 g of HZKQ-IB4A was dispersed in 600 ml of a 5% w/v aqueous zinc nitrate solution. The whole mixture was refluxed for four hours. After filtration, washing and drying the solid material was impregnated with 5% lanthanum. This was followed by calcination at 500°C for three hours. The material was allowed to cool to room temperature and pelletized without binder.

I) Sodium-exchanged catalyst plus stearic adic (Sterotex) 0.4 wt% Na-ZKQ-IB4A + stearic acid (Test no 8)

The sodium-exchanged catalyst with a sodium content of 0.4% by weight was mixed with stearic acid (5% by weight w.r.t. catalyst) and then pelletized. The pellets were calcined at 500°C for 3 hours to remove the lubricant or organic binder.

2.2 CHARACTERIZATION OF IRONBOROSILICATE ZEOLITES

A detailed account of the work done on the characterization of ZKQ-IB zeolites by the following techniques was given in our previous report (16).

- High resolution magic angle spinning NMR of ^{13}C, ^{27}Al, ^{11}B and ^{28}Si;
- X-ray diffraction for structure verification and for the determination of the relative degree of crystallinity;
- X-ray photon spectroscopy for the study of surface iron;
- elementary analysis for determining chemical composition and mole oxide ratios;
- n-pentane adsorption for determination of channel volume;

- thermal analysis for determination of the number of TPA^+ ions that can be accomodated per unit cell;
- electron microscopy for particle size determination and morphological study.

In the present work, therefore, characterization was limited to x-ray diffraction, elementary analyses, acidity measurement by ammonia chemisorption, electron microscopy and thermal analysis.

2.2.1 X-ray powder diffraction

We present in Figures 1 and 2 x-ray powder diffraction patterns of the base zeolite HZKQ-IB4A prepared in the previous project and of TPA-ZKQ-IB4A prepared in the present project in a batch 3.5 bigger than that of the previous project. Both x-ray diffraction patterns were similar save for the peaks at about 10 and 11.2A which were of lesser intensities for the zeolite precursor than for the calcined zeolite. Indeed, it is generally observed that the intensities of these two lines are lower for zeolite precursors than for those displayed by zeolites that have been calcined at temperatures that normally would not alter their structural integrity. Normally, minor shifts in interplanar spacings and variations in relative intensities may occur as a result of heat treatment or ion exchange. Table 2 shows the positions and the relative intensities of the peaks.

2.2.2 Elementary analyses

The various metals contained in each of the prepared catalysts were determined by inductively-coupled plasma emission spectrophotometry. From the results presented in Table 3 the following observations can be made:

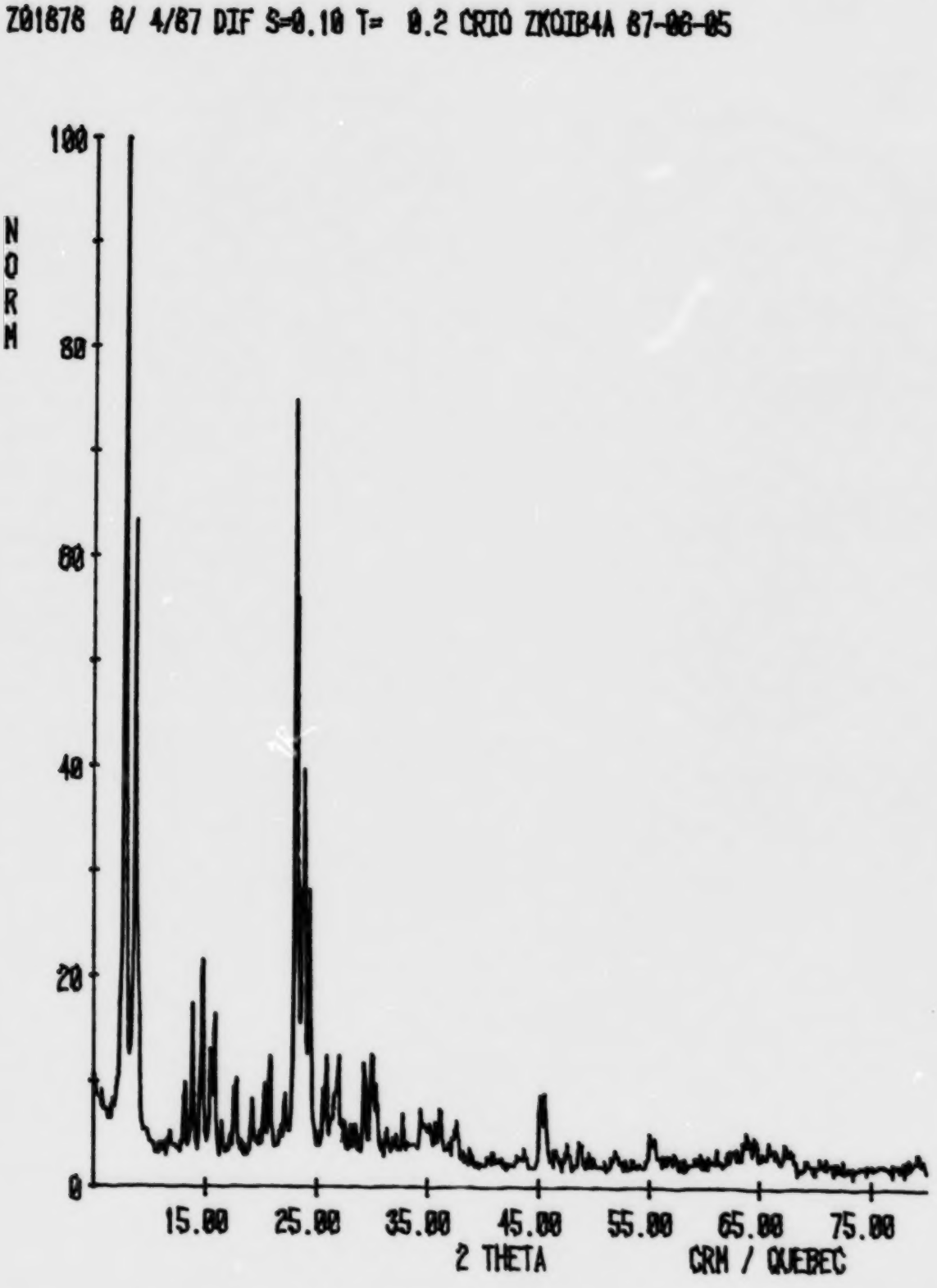


FIGURE 1: X-ray powder pattern of ZKQ-IB4A

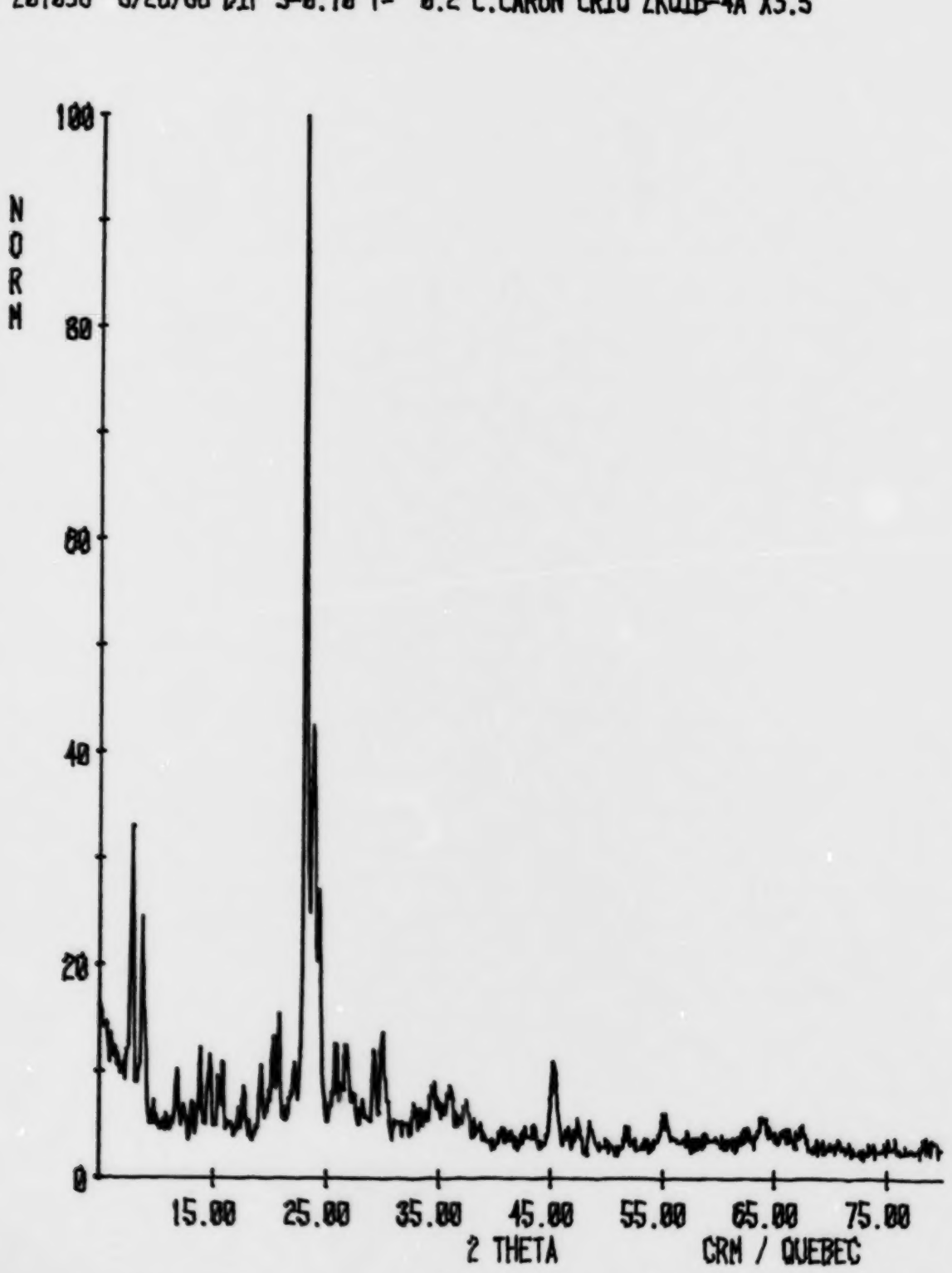


FIGURE 2: X-ray powder pattern of ZKQ-IB4A x3.5

TABLE 2: Typical x-ray diffraction

INTERPLANAR SPACINGS, d (A)	RELATIVE INTENSITY
11.2 ± 0.2	w - s
10.05 ± 0.2	w - ms
9.05 ± 0.15	vw
7.50 ± 0.15	w
7.13 ± 0.15	vw
6.71 ± 0.15	vw
6.40 ± 0.15	w
6.04 ± 0.1	w
5.7 ± 0.1	w
5.60 ± 0.1	vw
5.13 ± 0.1	vw
5.00 ± 0.1	w
4.62 ± 0.08	w
4.26 ± 0.08	w
4.02 ± 0.08	w
3.83 ± 0.05	vs
3.71 ± 0.05	s
3.65 ± 0.05	m - s
3.43 ± 0.05	w
3.33 ± 0.05	w
3.26 ± 0.05	vw
3.05 ± 0.05	w
2.99 ± 0.02	w
2.85 ± 0.02	vw
2.78 ± 0.02	vw
2.73 ± 0.02	vw
2.61 ± 0.02	vw
2.49 ± 0.02	w
2.39 ± 0.02	vw
2.00 ± 0.02	v - m
1.95 ± 0.02	vw
1.91 ± 0.02	vw
1.87 ± 0.02	vw
1.76 ± 0.02	vw
1.66 ± 0.02	vw

vs ..... very strong
s ..... strong
ms ..... medium strong
m .....medium
mw ..... medium weak
w ..... weak
vw ..... very weak

TABLE 3: Elementary analyses*

CATALYSTS	Fe	Na	Co	La	Zn
ZKQ4A (Test no 1)	10.3	0.18			
Co-ZKQ4A -(0.4Na+5%La) (Test no 3)	8.46	0.38	927 ppm	> 3	
Co-ZKQ4A-0.67Na(La) (Test no 7)	8.73	0.99	0.1	> 3	
Co-ZKQ4A-0.67Na(La) (Test no 12)	8.46	0.59	477 ppm	> 3	
Zn-ZKQ4A (La) (Test no 13)	8.62	0.06		> 3	0.32

* All values are quoted in wt% unless otherwise specified

- the vast difference in the residual sodium contents of ZKQ-IB4A prepared in the previous project and in this project can be attributed to more thorough washing and/or to the use of hot water for washing.
- The one-fold difference in the sodium and cobalt contents of the catalysts used in Tests no 7 and no 12 is attributable to different batches of catalysts. The lower Co and Na contents of the catalyst used in test no 12 seems to suggest that the number of exchangeable sites it has must be lower than that of other catalyst.

2.2.3 Electron microscope examination of Co-ZKQ-IB4A-0.67Na(La)

The electron photomicrographs shown in Figures 3, 4 and 5 are those of the cobalt sodium-exchanged and lanthanum-impregnated base zeolite taken at different magnifications on a JEOL scanning electron microscope at an accelarating voltage of 35 kV. At low magnification (x 2000) one can observe the near spherical particles whose dimensions ran from about 7 to about 13 microns. Smaller loose particles of different shapes ranging in size from less than 1 micron to about 4 microns and twinning of spherical particles can be readily seen as well. An examination of Figure 4 taken at a magnification of X 6000 shows that the spherical particle is composed of a multitude of agglomerated lathe-shape crystals stacked on top of each other. Figure 5 taken at still greater magnification (X 10 000) reveals that the dimensions of the near rectangular crystals have dimensions of about 1 x 0.2 x 0.05 micron (l x w x t).

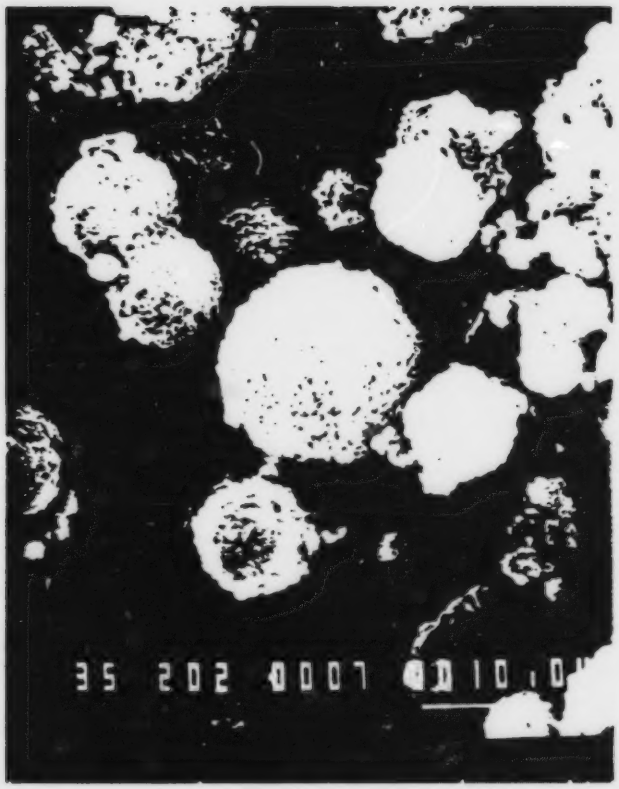


FIGURE 3

SCANNING ELECTRON PHOTOMICROGRAPH OF Co-ZKQ4A-0.67Na(La)

(x 2000)

Scale: 1 micron = ? mm

FIGURE 4

SCANNING ELECTRON PHOTOMICROGRAPH OF Co-ZKQ4A-.67Na(La)

(x 6000)

Scale: 1 micron = 5 mm

FIGURE 5

SCANNING ELECTRON PHOTOMICROGRAPH OF Co-ZKQ4A-.67Na(La)

(X 10 000)

Scale: 1 micron = 10 mm

2.2.4 Acidity of base zeolite

The surface acidity of the base zeolite which in effect determines its activity was determined by ammonia chemisorption technique (45) using thermal conductivity detector whose response has been shown to vary linearly with the quantity of ammonia (18).

The results obtained for different batches of the base zeolites, H-ZSM-5, ZMQ-TB4B (46), TS-1 (47) and gasoline-producing ZKQ-IB5 are shown in Table 4. A typical example of the method used for calculating the number of moles of ammonia adsorbed per gram of the catalyst is shown in Table 5 wherein the detector response for three consecutive pulse injections of 0.25 cc of NH_3 do not differ from each other by 1%. At this point the catalyst surface is considered to be completely saturated with ammonia and pulse injection of the gas is stopped.

The results of surface acidities of the various zeolitic catalysts clearly indicate that HZSM-5 with a SiO_2/Al_2O_3 ratio of about 40 has the highest acidity followed in decreasing order of magnitude by ironborosilicate, titanoborosilicate and titanosilicate. The ironborosilicate with the least acidity (1.608372×10^{-4} mole of NH_3/g) happens to be the base zeolite which contained a relatively high sodium content (0.53 wt%) compared to that of the base zeolite used in Test no 1 (0.18 wt% Na and acidity of 2.758797×10^{-4} mole NH_3/g).

As expected, the titanosilicate zeolite, TS-1, showed the least acidity which probably originates from the presence of impurities. Theoretically it should not possess any exchangeable sites just like silicalite.

TABLE 4: Surface acidities of catalysts by ammonia chemisorption

SAMPLES	HZKQ-4A [1]	HZKQ-4A [2]	HZKQ-4A [3]	HZKQ-IB5 [4]	HZSM-5 [5]	TS-1 [6]	ZMQ-TB4B [7]
Moles NH_3 adsorbed per gm of catalyst ($\times 10^{-4}$)	1.608372	2.758797	2.668761	3.345754	5.771747	0.968386	2.024489

1. HZKQ-IB4A prepared in our previous project
2. HZKQ-IB4A prepared in this project in batches 3.5 times bigger than in previous project (Test no 1)
3. HZKQ-IB4A prepared in this project in batches 3.5 times bigger than in previous project (Test no 12 and 13)
4. HZKQ-IB5 crystalline ironborosilicate catalysts which produced only gasoline
5. HZSM-5 with 0.3% Ni and having a SiO_2/Al_2O_3 ratio of about 40
6. TS-1 is a crystalline titanosilicate zeolite of the ZSM-5 type
7. ZMQ-TB4B is a titanoborosilicate zeolite which has converted methanol directly to high octane gasoline

TABLE 5: Method of calculating moles of NH_3 absorbed/gram of catalyst

HZQK-IB4A	
RUN AREA	DELTA AREA
4 335	2 534 958
2 413 870	1 254 423.3
2 549 610	0
2 529 430	0
2 538 840	0
average	sum
2 539 293	2 660 382

P = 757.6 mm Hg V = 0.25 cc

T = 393.15 K R = 62 400 mm Hg cc/mol*K

m = 0.05029 g

n = PV/RT

n = 7.7203551E-06 moles

moles adsorbed = sum * n/average
= 8.088502E-06 moles

The moles of NH_3 adsorbed/gram of catalyst = 1.608372E-04 mol/g

2.2.5 Thermal analysis

Thermal differential analysis was carried out on a sample of HZKQ-IB4A which was heated from room temperature to 950°C in a cell. Alpha alumina was used in the reference cell of the Mettler Thermal Analyser. No endotherms or exotherms were detected, thereby indicating that the zeolite was thermally stable at 950°C. Had there been structural collapse or crystalline phase change this would have been detected. For instance, structural collapse of the zeolite would have released heat, which would appear as an exotherm. As shown in Appendix D, an x-ray powder diffraction pattern taken on the sample on which DTA was performed was similar to the one provided by a fresh sample of the zeolite.

3.0 TESTING UNIT

A schematic diagram and a photo of the synthesis gas conversion testing unit consisting among other things of two similar independant, fixed-bed tubular reactors are shown in Figures 6 and 7 respectively. The reactor itself was a half-inch o.d. 316 stainless steel tube with a 1/16 inch o.d. inside thermowell, which allowed the positioning of three thermocouples at the top, middle and bottom of the catalyst bed. The reactor was surrounded by a thick aluminium sleeve which helped to control the temperature to within ±1°C. Heat was supplied by a small Lindberg furnace. The temperature variation along the bed was found to be within ±2°C. It can thus be said that all test runs were carried out under essentially isothermal conditions. The maximum volume of catalyst that can be tested in the reactor is about 15 ml. The mass flow controllers were calibrated prior to each test.

Feed synthesis gas obtained by mixing hydrogen and carbon monoxide in the desired ratio was sampled via a «bypass» circuit and analysed by on-line g.c. once a day. Light product gases and unconverted synthesis gas were analysed once every two hours during the test run. Both liquid products from the heated (80°C) and non-heated traps were collected once every two days. Analysis of product liquid hydrocarbons provided both qualitative and quantitative data on the various components contained therein. With the aid of a computer software which we have developed these and other data were used to calculate the material balance for each test run.

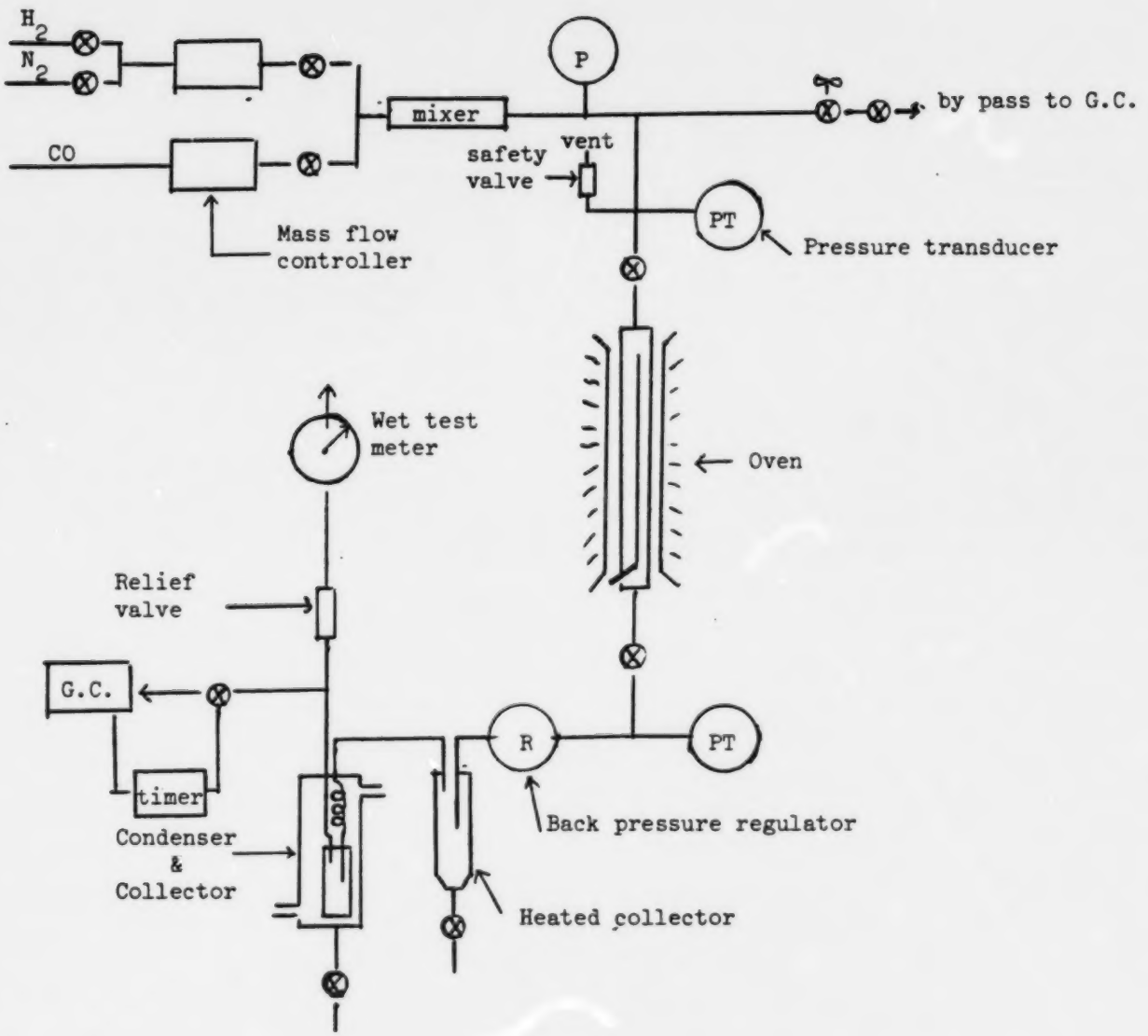


FIGURE 6: Schematic diagram of the microreactor system

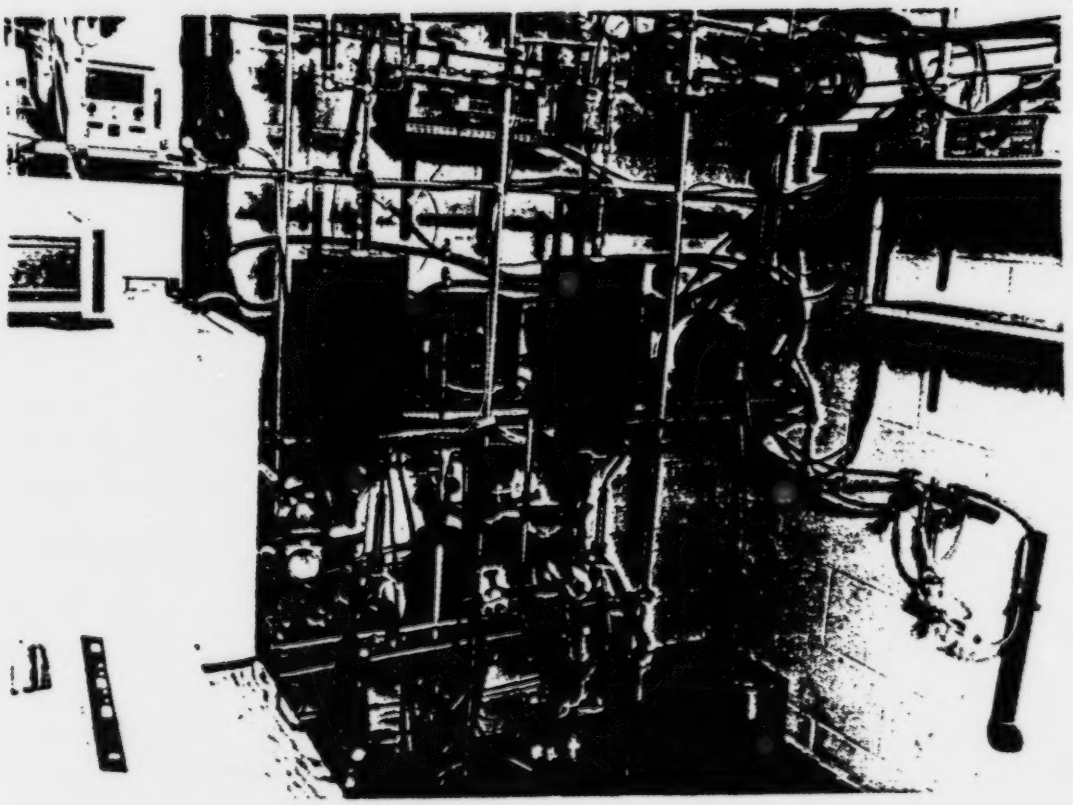


FIGURE 7: Catalysts testing unit with 2 small tubular fixed-bed reactors in parallel

3.1 INSTRUMENTAL ANALYSIS

C_1 to C_5 hydrocarbons as well as H_2, CO, CO_2 and N_2 were analysed on an on-line Hewlett Packard gas chromatograph, model HP5790A, equipped with the following columns:

1. A 5 ft column packed with 30% DC 200 silicone oil on 80/100 mesh chromosorb PAWIB placed in series with a 24 ft column packed with 16% bis-2-methoxy-ethyl adipate on 80/100 mesh chromosorb PAW was used to analyse C_3 to C_5 hydrocarbons.

2. A 6 ft Porapak Q 80/100 mesh was used for the analyses of CO_2, C_2H_4 and C_2H_6.

3. A 10 ft Molecular Sieve B 45/60 mesh column was used to analyse N_2, CH_4 and CO.

Standards comprising of pure gas mixtures purchased from Matheson were used to calibrate instrument response. The composition of the liquid organic phase characterized by its PONA content (Parrafins, Olefins, Napthlenes, Aromatics) was determined on a Hewlett Packard gas chromatograph, model HP5880, equipped with a 50 meter capillary fused silica column and a Hewlett Packard software for PONA analysis.

The PONA calibration table supplied by Hewlett Packard was used to verify peak positions on the chromatogram in terms of retention times. Due to the limitation of the computer programs, peaks higher than C_{13} could not be quantified. Oxygenates such as alcohols and acetone were analysed by GC on a carbowax column.

The simulated distillation was also run on the same HP5880 with the software and calibration mixtures supplied by HP. The column used was:

1/8 x 20 inch stainless steel, 10% UC-W982 on 80/100 mesh chromosorb P-AW.

The HP Simulated Distillation Program calculates and provides a printed report of the boiling point distribution of hydrocarbon fractions. A correlation between boiling points and time of elution provides a basis for the method. A mixture of normal paraffins up to C_{40} obtained from the Ultramar Refinery in St-Romuald was used for calibration. Samples of diesel purchased from a gas station were used as a standard to calculate the diesel fraction in the samples collected from the reactor. The HP programme automatically identifies the peaks, calculates the curve-fit constants for boiling point as a function of retention time, and stores these constants for later use.

The HP program provides two calculation procedures: Normalization and Internal Standard. The Normalization procedures follows exactly the ASTM Method D 2887. In this project the Normalization procedure was used to obtain the boiling point distribution.

3.2 TESTING OF PREPARED CATALYSTS

The volume of catalyst in the form of cylindrical pellets measuring 1/8 inch x 3/16 inch used in each of the tests was 8 ml. Except for the catalyst used in Test no 8 which was pelletized with 5% Sterotex, no binder or lubricant was used in the pelletization of all the other catalysts.

Total carbon analysis was performed on each used catalyst which was ground well beforehand. Catalyst fines were not observed.

3.2.1 Reduction conditions

As mentioned earlier ZKQ-IB4A base catalyst may well be considered as a crystalline ironborosilicate zeolite on which iron oxide is so well dispersed that it would be virtually impossible to separate both entities from each other. Unmuth et al (48) studied the reduction of Fe_2O_3-SiO_2 by temperature-programmed reduction and found that the TPR profile showed two peaks at about 307°C and 447°C which they attributed respectively to the following two reactions:

At 307°C: $H_2 + 3\ \alpha - Fe_2O_3 \rightarrow 2Fe_3O_4 + H_2O$
At 447°C: $4H_2 + Fe_3O_4 \rightarrow 3\alpha\text{-}Fe + 4H_2O$

It is known that it is difficult to prepare highly dispersed supported iron catalysts; highly dispersed iron cannot be completely reduced to the metal but poorly dispersed iron oxide can be (39). Impregnated iron catalysts are more easily reduced in the presence of Pt or Ru (49).

Among the usual transition metals used in the F-T synthesis, iron possesses the greatest tendency to produce elemental carbon, which may clog fixed bed reactors and penetrate into iron crystallites where it can grow to such an extent as to cause the disintegration of the catalyst particles to fines. Carbon deposition is usually not a serious problem below 275°C. At 325°C, however, water or hydrogen-containing molecules increase the rate of the Boudouard reaction ($2CO \rightarrow C+CO_2$). According to Shultz et al (50), the carbon deposited by the action of CO or synthesis gas on various forms of iron consti-

tutes a long-life catalyst whose activity is attributed to the cristallites of iron embedded in the carbon.

In light of the foregoing and considering that the ZKQ-IB4A base catalyst is in fact a supported iron catalyst wherein the iron is highly dispersed in a matrix of silica, we opted for a reduction procedure which involved the following steps:

- Reduction with a mixture of 75% H_2 and 25% He at 450°C, 1 atmosphere and space velocity of 1000 h^{-1} for 30 hours. The heating rate was set at 3°C/min.

- Carbiding at 325°C with synthesis gas (H_2:CO of 1:1) at 1 atm and gas hourly space velocity of 1000 h^{-1} for 10 hours. Carbiding such freshly reduced catalyst would produce cementite, elemental carbon and magnetite in addition to Hagg carbide (39), which should be the major phase.

Data obtained from a study conducted by Anderson et al (39) using water as the oxidant have shown that reoxidised iron catalyst is much easier to reduce than the raw or the partly reduced catalyst. Pommier et al (51) reported that the F-T reaction carried out at 250°C on a silica supported preoxidised iron (10% Fe) aerogel catalyst showed a particularly high activity and stability with time on stream. The spent catalyst was found to be uncarburised and in the oxidised ferroferric state (Fe_3O_4) with only a small amount of inactive carbon deposit. When the same catalyst was prereduced to metallic iron it deactivated with time on stream and it was found to contain iron carbides and inactive carbon deposit. The activity of the preoxidised catalyst was much higher than that of the prereduced catalyst. Assuming that CO adsorbs dissociatively on the preoxidised catalyst, the authors (52) have suggested that

the higher activity of the catalyst could be attributed to the formation of a redox system involving Fe_2O_3/Fe_3O_4 which promotes the dissociation of CO into active carbon via the following reaction mechanism:

$Fe_2O_3 + (CO+H_2) \rightarrow Fe_3O_4 + (CO_2 + H_2O)$ stabilized
$2Fe_3O_{4(s)} + CO \rightarrow 3Fe_2O_{3(s)} + C_{(active)}$
$C_{(active)} + H_2 \rightarrow -CH_2-$

They concluded that the amount of active carbon is high and that of inactive carbon is low on preoxidised catalyst whereas the reverse applies to the prereduced catalyst. This means that the high amount of active carbon on the proxidised catalyst accounts for its particularly high activity.

Manning and Reid (53) have reported that carbon deposit does not take place on magnetite and iron carbides.

In light of the foregoing the catalyst used in Test no 9 was accordingly preoxidised in accordance with the following procedures in an attempt to improve its activity and stability.

Step 1

Reducing gas ..... H_2
Temperature ..... 400°C
Pressure ..... 1 atm
GHSV ..... 1000 h^{-1}
Duration ..... 24 h

Step 2

Gas used to flush catalyst bed ..... He
Temperature ..... 300°C
GHSV ..... 1000 h^{-1}
Pressure ..... 1 atm
Duration ..... 2 h

Step 3

Gas used ..... O_2 and He (50/50)
Temperature ..... 300°C
GHSV ..... 1000 h^{-1}
Duration ..... 3 h

Step 4

Same as step 2

Step 5

Line out the reactor for synthesis reaction as per the conditions given below

3.2.2 <u>Operating conditions for F-T synthesis</u>

Unless otherwise specified the reaction conditions employed in all of the tests were as follows:

Weight of catalyst, g 5-7
Volume of catalyst, ml 8
Temperature, °C 300
Pressure, kPa 1 020
Gas Hourly Space Velocity, h^{-1} 300
Duration, h 366

3.2.3 Results and discussion

In total thirteen tests were carried out. As mentioned earlier, with the exception of Test no 9 all the remaining tests were conducted under the same activation and synthesis conditions. No sign of deactivation of the catalysts or of reactor plugging was detected at the conclusion of all the tests. The results obtained in each test will be discussed.

3.2.3.1 Test no 1 (ZKQ-IB4A base zeolite)

As mentioned earlier the base zeolite was prepared in batches 3.5 times bigger than those in the previous project. The object of this test was therefore to verify whether or not the performance of this catalyst would be similar to that found for a similar catalyst in the previous project.

From a comparison of the results of the two tests obtained at 96 hours on stream presented respectively in Tables A1 and A2 in Appendix A, the following statements can be made:

- In terms of H_2 and CO conversion the activity of the present catalyst was higher than that of the previous catalyst; however, both catalysts showed moderate activities.

- Selectivity to liquid hydrocarbons was definitely much higher in the present test.

- PONA results showed that the liquid product obtained in this test contained much less paraffins (33.42% vs 54%), significantly more olefins (32.32% vs 26.52%), much more aromatics (22.97% vs 10.75%) than in the liquid product of the previous test; moreover, hydrocarbons with carbon number greater than 13 were not detected in this test. This is contrary to what has been observed in the previous test run which produces n-paraffins up to C_{20}.

The difference in behaviour of these two catalysts is attributable to the higher acidity of the present catalyst on account of its lower residual sodium content as shown in Table 6. It is known that high acidity is required for aromatisation and isomerisation reactions, whereas low acidity or high sodium content do not favour these two reactions but tend to favour the production of higher molecular weight linear paraffins. This is amply demonstrated by these two catalysts which had different residual sodium contents.

TABLE 6: Na and Fe contents in catalyst ZKQ-4A

	Na (wt%)	Fe (wt%)
After 1st exchange	0.18	9.40
After 2nd exchange	0.15	9.60
After 3rd exchange	0.15	10.40
After 4th exchange	0.18	10.30
ZKQ-4A (from previous project 16)	0.53	10.63

This difference in the residual sodium content is directly related to the easier removal of sodium with hot water than with cold water during washing of the base zeolite. In practice it would appear that the control of residual sodium is difficult. One way to obviate this difficulty would be to use ammonium hydroxide as the base in the reaction mixture not only to control the pH and to act as counterions but also to do away with the need to carry out the ion exchange with ammonium chloride solution. The calcined zeolite would be in the acid form and sodium-free. It can then be doped with sodium or potassium.

As can be seen in Table 6 the sodium and iron contents are only slightly affected by the number of exchange with ammonium chloride at 90°C. It is highly possible that the difficultly leached sodium is associated more with iron oxide in which it is occluded rather than with the zeolite.

3.2.3.2 Tests no 6 and 7 of cobalt-exchanged and Na, La-impregnated base zeolites Co-ZKQ-IB4A-0.4 Na(La) and Co-ZKQ-IB4A-0.67 Na(La)

The results of these two tests are presented in Tables A7 and A8. The two catalysts differ from each other only in regard to their sodium contents which were 0.4 and 0.67 wt%. As observed in Test no 1, we would expect different behaviours from these two catalysts in so far as syngas conversion, selectivity to C_{5+} hydrocarbons and the nature of these hydrocarbons are concerned. However, in order to avoid unnecessary repetitions, we have deemed it necessary for the purpose of a detailed discussion to focus our attention on the results obtained from the testing of CO-ZKQ-IB4A-0.67 Na(La) which, according to us, typifies all modified ZKQ-IB4A catalysts dealt with in this project. Fur-

thermore, this catalyst produced the most interesting results in so far as liquid hydrocarbon and distillate yields are concerned.

In Figure 8, CO_2, CH_4 and C_2H_6 selectivities and unreacted H_2 and CO are plotted against time-on-stream. After an initial drop from 44% at the outset of the reaction to 37% after 30 hours on stream, CO_2 selectivity remained almost constant at this value over the entire duration of the run which was 336 hours. During the first 48 hours, CH_4 and C_2H_6 selectivities remained practically constant at 5 wt% and 2 wt%, respectively. As shown in Figure 9, H_2 conversion levelled off at 57 wt% after increasing in the first 120 hours. CO conversion stabilized at 61 wt% after about 30 hours. In terms of synthesis gas conversion, this catalyst showed moderately good activity. As can be seen in Figure 10, selectivities to H_2O (6 wt%) and CO_2 (36 wt%) which are respectively reactant and product in the water gas shift reaction remained practically constant during the entire run and they were relatively not high especially when they are compared with those of Test no 5, which gave corresponding selectivities of 6.75% and 50.53%. Since both catalysts had the same sodium contents, it would appear that either Co or La or both depress the internal shift reaction to some extent.

FIGURE 8: Co-ZKQ-4A-0.67 Na (La)

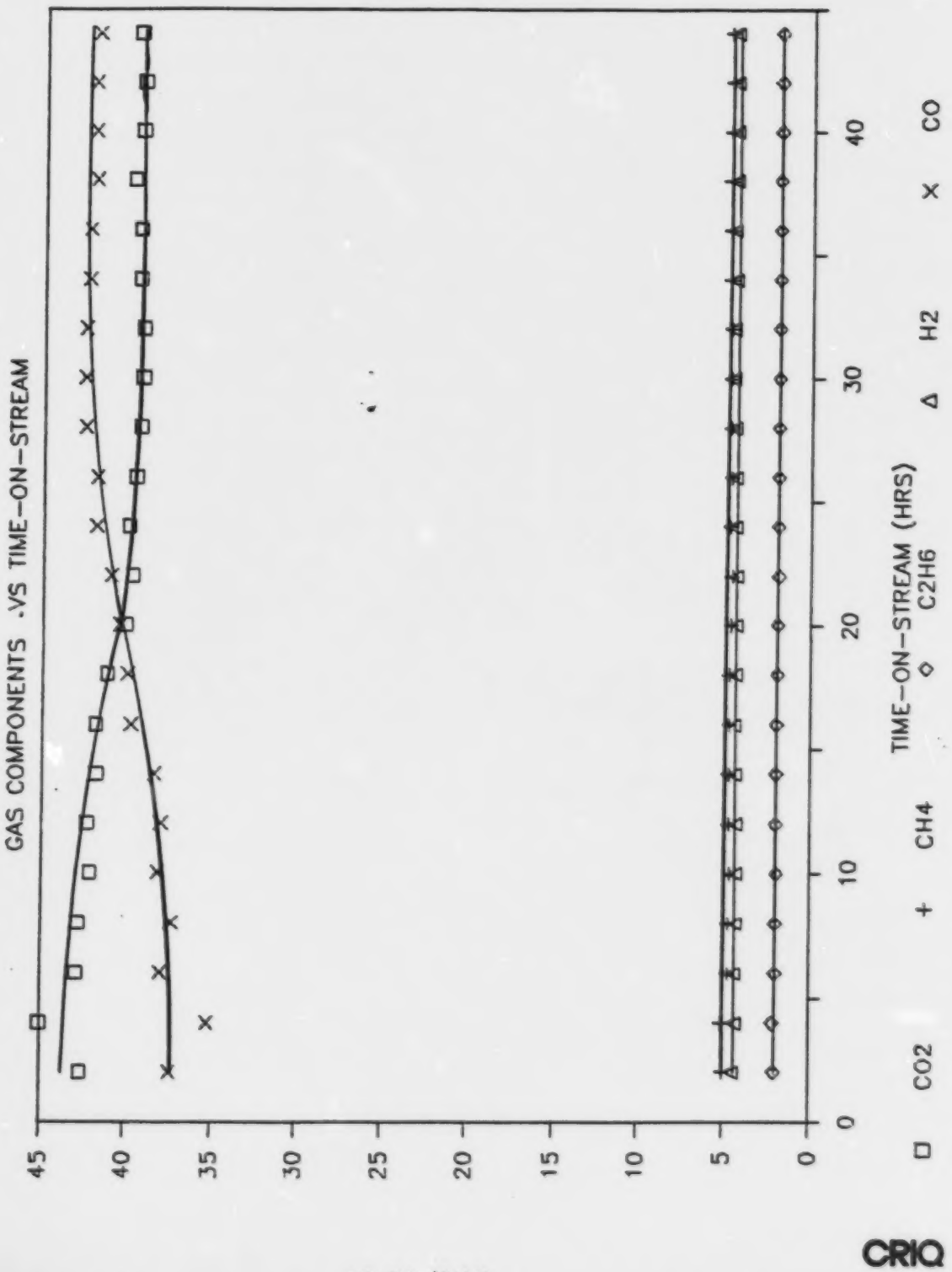
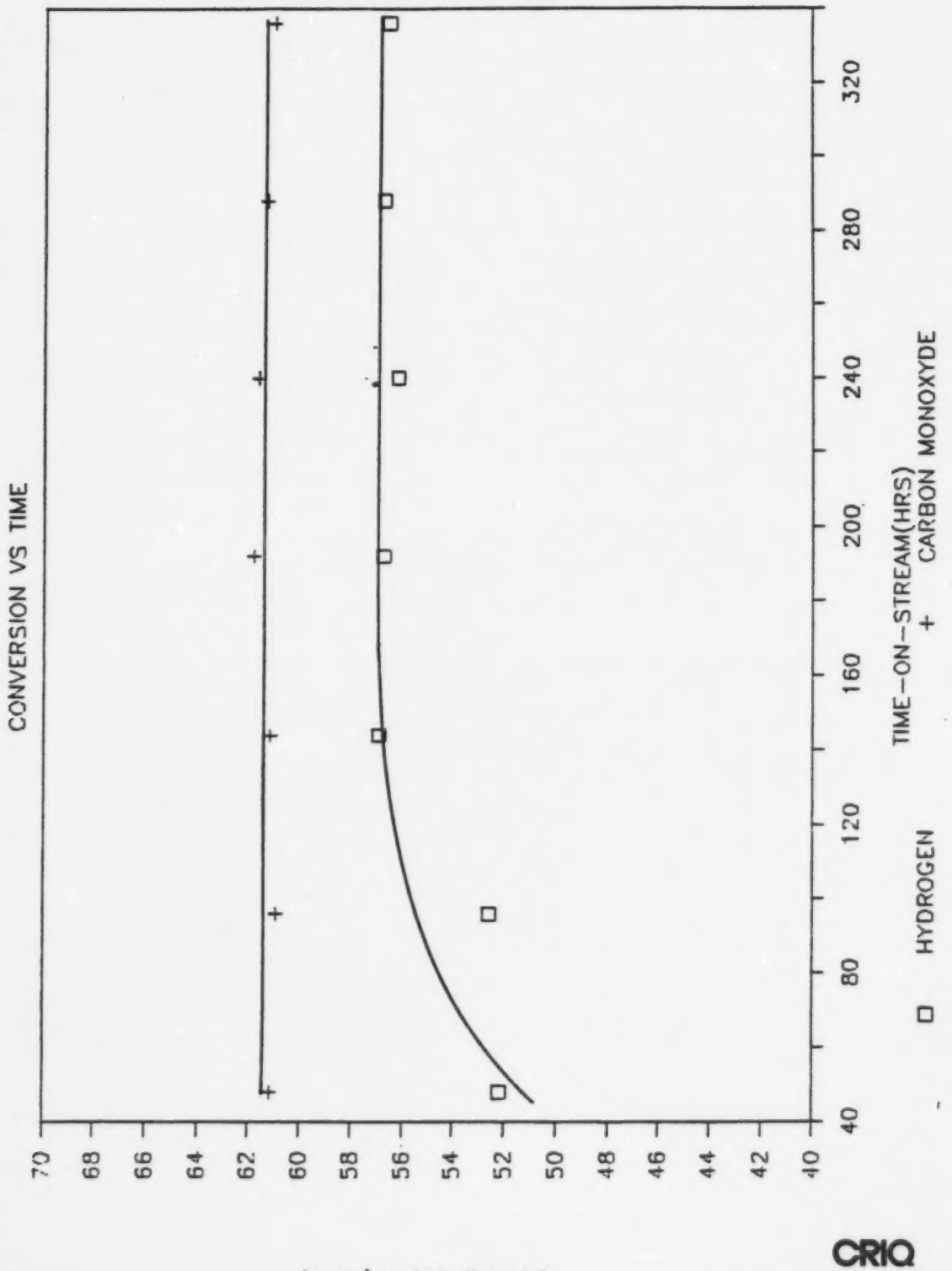
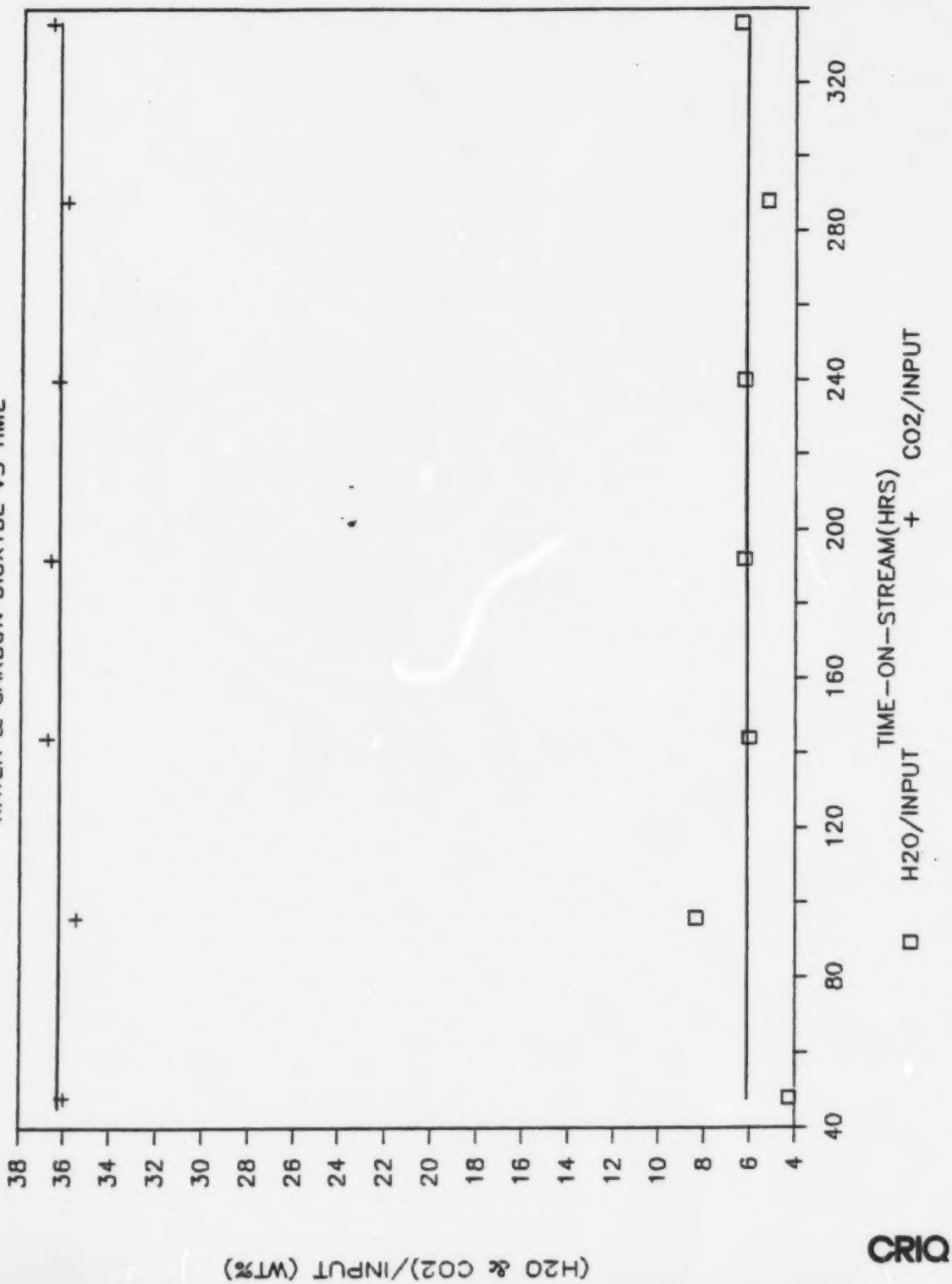


FIGURE 9: Co-ZKQ-4A-0.67 Na(La)



CRIQ

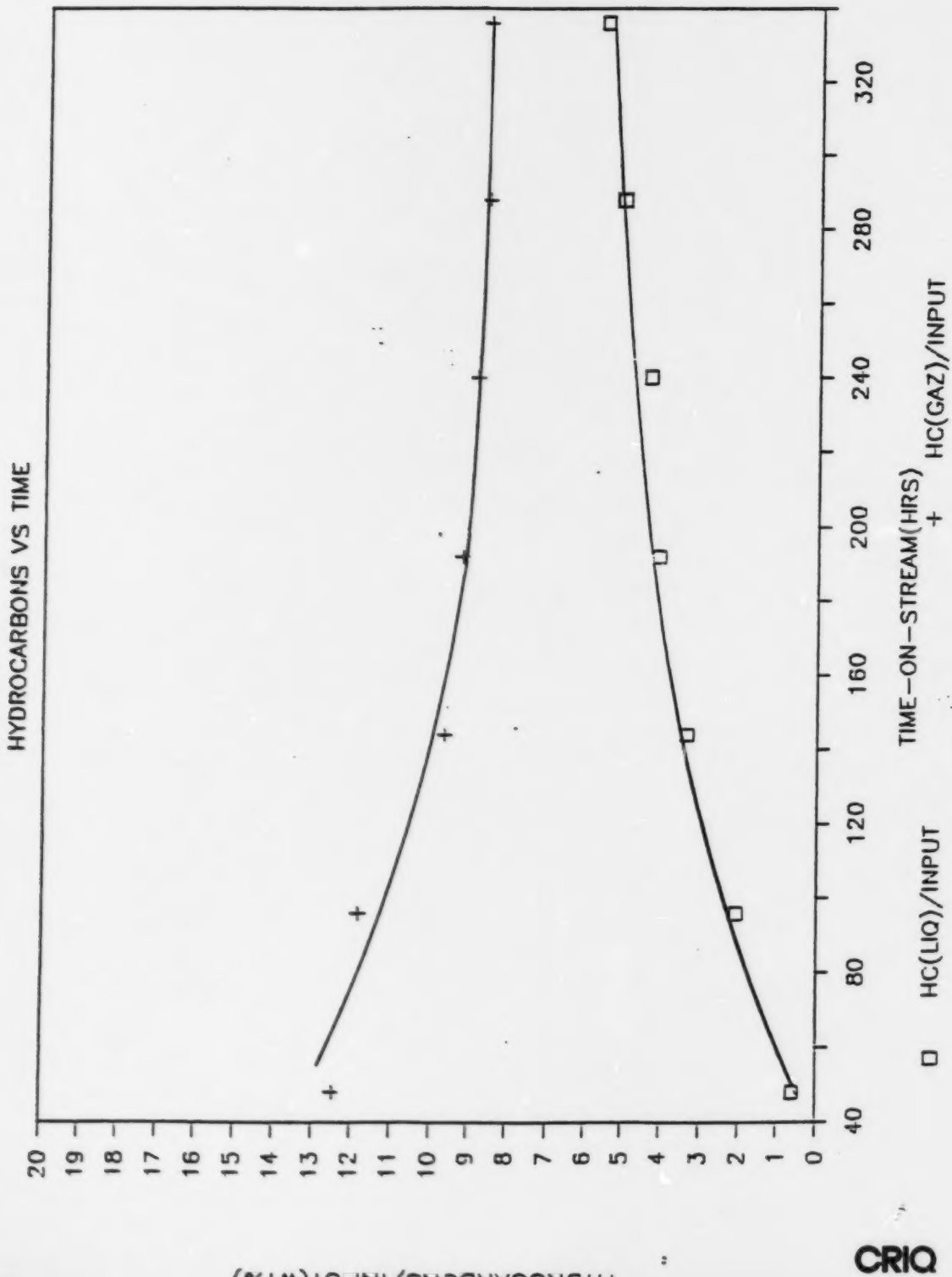
FIGURE 10: Co-ZKQ-4A-0.67 Na(La)



Based on a synthesis gas conversion of about 60 wt%, total hydrocarbon selectivity remained practically constant a little above 13% over the entire run. As can be seen in Figure 11, C_5+ hydrocarbon selectivity increased from an initial low of 0.6% to 5.6% at the conclusion of the test at the expense of gaseous hydrocarbons whose selectivities decreased from an initial high of 13% to 8.5%. This trend is selectivity change with time-on-stream is better illustrated in Figure 12 where selectivity as defined by $(C_1-C_4)/C_5+$ is plotted against time. That figure clearly shows a decline in selectivity to light hydrocarbons with time and a significant increase in the production of C_5+ hydrocarbons. At the conclusion of the test liquid hydrocarbons constituted about 42.5 wt% of the total hydrocarbons, compared to 26 wt% for Test no 5 in which the same base catalyst containing 0.67 wt% of Na was used but it did not contain Co and La. This can only mean that either Co exchange or La impregnation, or both promote the production of liquid hydrocarbons at the expense of gaseous hydrocarbons.

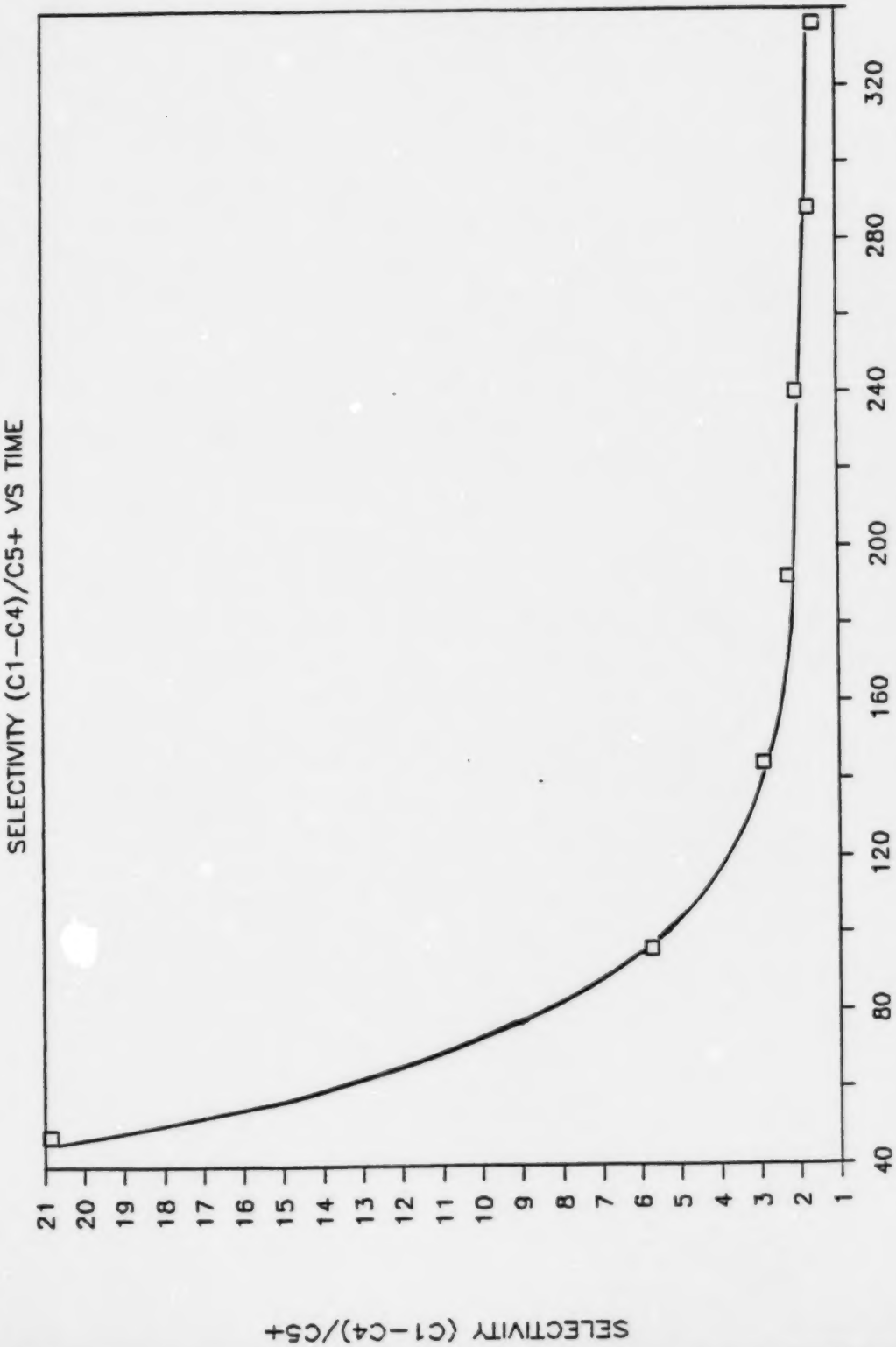
Changes in the PONA contents of the liquid hydrocarbons with time-on-stream are shown in Figure 13. While the paraffins content of 43.5% did not show any significant changes during the run, both naphtenes and aromatics contents decreased from 12 to 9% and from 10.7% to 8.5% respectively over a period of about 300 hours. Over the same period there was an increase in the olefins content from 35 to 39% which represents an increase of about 11.4% with respect to the initial content. Such an increase has not been observed in most of the other tests.

FIGURE 11: Co-ZKQ-4A-0.67 Na(La)



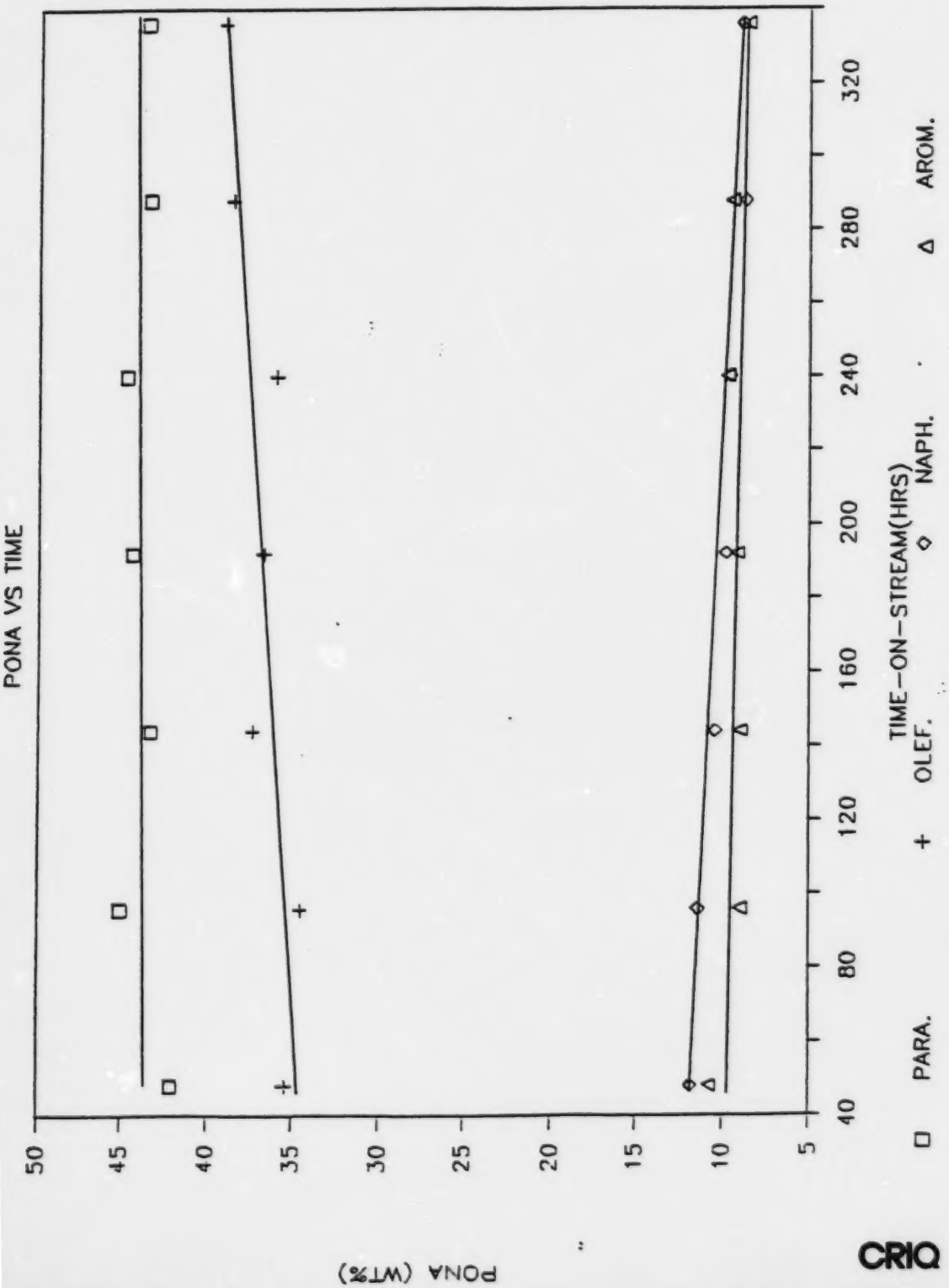
CRIQ

FIGURE 12: Co-ZKQ-4A-0.67 Na(La)



CRIQ

FIGURE 13: Co-ZKQ-4A-0.67 Na(La)



The gas chromatograms of the liquid hydrocarbons sampled after 48 and 336 hours on stream are included in Appendix B in order to illustrate the progressive increase of C_{13} to C_{27} hydrocarbons with time. From the simulated distillation curve of the liquid product shown in Figure 14 we can calculate the fractions of gasoline, diesel and wax. The results are shown in Table 7.

TABLE 7: Simulated distillation

% vol. with boiling points up to 200°C (gasoline)	53
% vol. with boiling points up to 405°C (diesel)	44
% vol. with boiling greater than 405°C (wax)	3
Ratio of Gasoline: Diesel	1.2

When the distillation curve is compared directly with that of diesel purchased from a gas station, the calculated fractions of the three components are as shown in Table 8.

TABLE 8: Simulated distillation with commercial diesel as standard

	TEST NO 7 LIQUID HYDROCARBONS	COMMERCIAL DIESEL
Vol. % with boiling points up to 125°C	22	0
Vol. % with boiling points from 125 to 405°C	75	100
Vol. % with boiling greater than 405°C	3	0
Ratio of Gasoline:Diesel	0.29	

SIMULATED DISTILLATION PROFILE

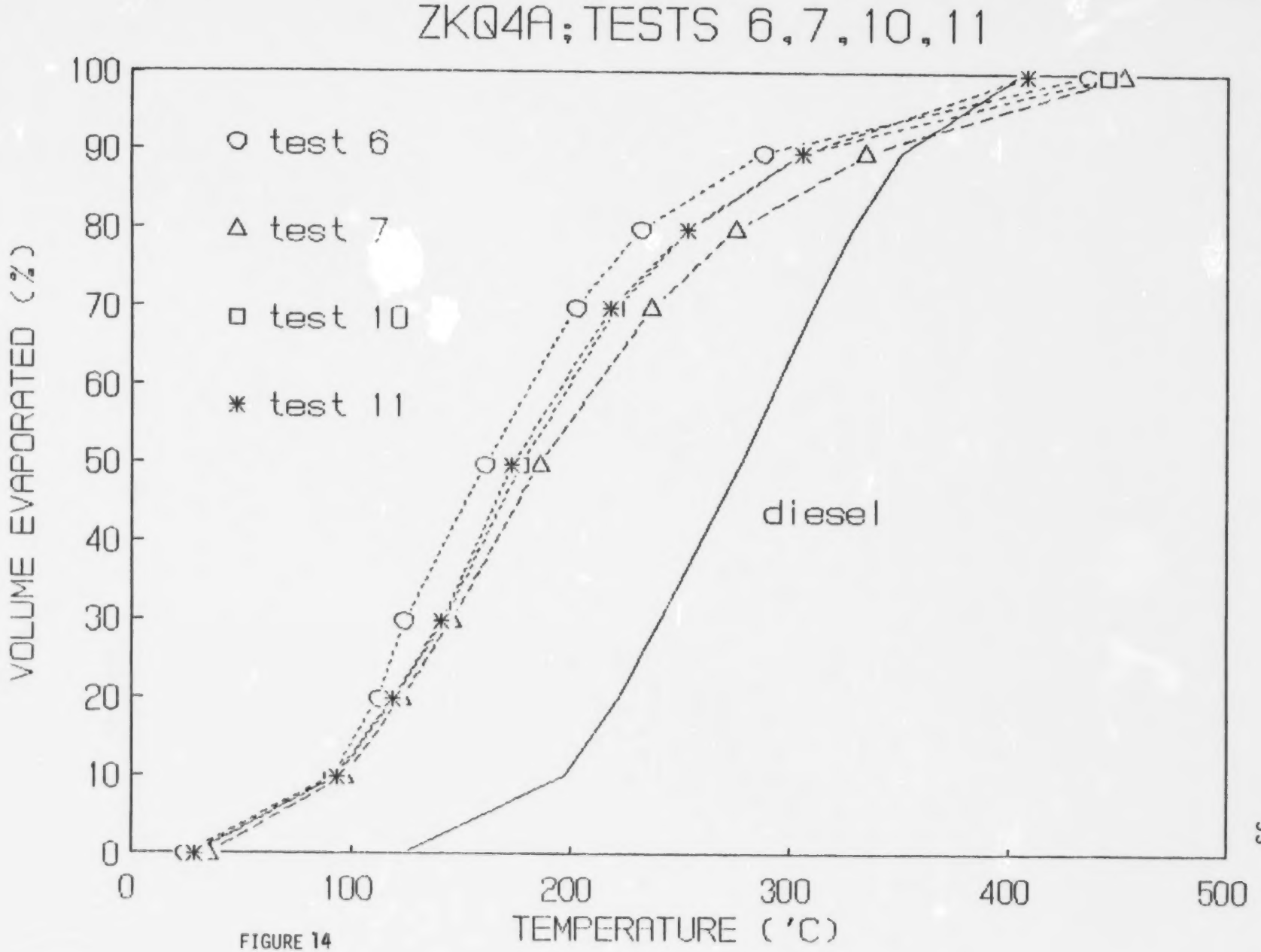


FIGURE 14

MAT-88-032

As seen in Table 8, this method of computing based on the direct comparison of the distillation curve of the liquid sample with that of commercial diesel gives a diesel to light gasoline ratio of 3.4. This method would be acceptable if the light portion of the liquid sample were high in linear paraffins and low in aromatics. However, it appears that most of the aromatics are highly substituted with boiling points up to about 175°C. GC/FTIR analysis of the liquid hydrocarbons obtained from a similar catalyst but containing less sodium has shown that most of the alkanes were unbranched. The results are presented in Table 9.

From an examination of the results of Tests no 6 and 7 shown in Tables A7 and A8 respectively the following remarks can be made:

- Differing only in their sodium contents both catalysts exhibited good synthesis conversion.

- As expected, the catalyst with lower sodium content used in Test no 6 (0.4% Na) showed higher syngas conversion than the catalyst with higher Na content (0.67%) used in Test no 7. Furthermore, it led to the production of liquid hydrocarbons which were more olefinic and less paraffinic in nature.

- As mentioned earlier, a shift in the product distribution to higher molecular weight hydrocarbons is observed when the catalyst is doped with increasing amount of sodium. It is therefore not surprising to observe greater C_{13}-C_{24} hydrocarbons selectivity over Co-ZKQ-IB4A-0.67% Na(La) than over Co-ZKQ-IB4A-0.4% Na(La).

- Although the overall syngas conversion was lower in Test no 7, C_5+ hydrocarbons selectivity was higher than in Test no 6 (42.62% vs 34.50%). This is also reflected in the simulated distillation curves shown in Figure 14. Furthermore, C_1-C_4 hydrocarbons selectivity was on the whole lower in Test no 7 which is attributables again to the higher Na content. It is noteworthy that formation of oxygenates is promoted by alkali metals.

In conclusion, the results of these two tests do confirm the fact that both syngas conversion and product distribution are profoundly influenced by the concentration of sodium in the catalyst.

TABLE 9: GC/FTIR analysis of C_5+ hydrocarbons

ECHANTILLON A					
PIC NO	TEMPS RETEN	C NO	FONCTION	IDENTIFICATION	COMMENTAIRES
1	12.63	C5	Alcane	Pentane	Confirme par standard
2	13.59	C5	Olefine	2-Pentene	Epa vapor phase library
3	15.12	C5	Olefine	2-Butene, 2-Methyl	Epa
4	25.16	C6	Alcane	Hexane	Epa
5	20.06	C6	Olefine	2-Pentene, 2-Mcthyl	Epa
6	27.47	?		May be hexene	
7	31.53	?	Alcane	Pentane, 3-methyl	Spectre faible
8	32.94	?			
9	33.85	?			
10	37.01	C7	Alcane	Heptane	Confirme par standard
11	38.02	?			
12	38.36	?			
13	44.40	C8	Olefine	2-henexe, 2.5-dimethyl	Epa
14	44.96		Olefine	Probablement un autre hexene substitute	
15	45.87		Alcane	Pentane, 3-ethyl ou heptane 3-3-dimethyl	
16	48.86	?			
17	49.36	C8	Alcane	Octane	Confirme par standard
18	56.59	?			
19	57.26	?			
20	60.03	C9	Alcane	Nonane	Confirme par standard
21	65.05	?			
22	65.33	?			
23	65.84	?			
24	68.10	C10	Alcane	Decane	Confirme par standard
25	73.12	?			
26	75.49	C11	Alcane	Hendecane	Confirme par standard
27	80.34	?			
28	80.79	?			
29	81.98	?			
30	85.36	C12	Alcane	Dodecane	Confirme par standard
31	100.31	C13	Alcane	Tridecane	Confirme par standard
32	110.19	C14	Alcane	Tetradecane	Confirme par standard
33	115.49	C15	Alcane	Pentadecane	Confirme par standard
34	119.44	C16	Alcane	Hexadecane	Confirme par standard
35	122.43	C17	Alcane	Pentadecane	Confirme par standard
36	125.08	C18	Alcane	Octadecane	Confirme par standard
39	127.62	C19	Alcane	Nonadecane	Confirme par standard

TABLE 9: GC/FTIR analysis of C_5+ hydrocarbons (cont'd)

ECHANTILLON La/Co 2A					
PIC NO	TEMPS RETEN	C NO	FONCTION	IDENTIFICATION	COMMENTAIRES
1	32.89	?			
2	33.85	?			
3	36.84	C7	Alcane	Heptane	Confirme par standard
4	42.42	?			
5	44.40	?	Olefine	2-Hexene, 2.5-Dimethyl 2.3-dimethyl-2-pentene	
6	44.96	C8	Alcane	2-Methyl heptane	
7	45.87		Alcane	Pentane, 3-ethyl ou heptane 3-3-dimethyl	
8	48.74	?			
9	49.36	C8	Alcane	Octane	Confirme par standard
10	56.59	?	Alcane	2-Methyl heptane ???? Pic 6	
11	57.26	?			
12	58.50	?			
13	60.03	C9	Alcane	Nonane	Confirme par standard
14	64.64	?			
15	65.16	?			
16	65.44	C10	Alcane	Methylnonane	Aldrich
17	65.90	?			
18	68.21	C10	Alcane	Decane	Confirme par standard
19	72.16	?			
20	72.38	?			
23	75.60	C11	Alcane	Hendecane	Confirme par standard
24	80.40	?			
25	80.85	?			
26	81.24	?			
27	81.92	?			
28	85.47	C12	Alcane	Dodecane	Confirme par standard
29	92.08	?			
30	92.47	?			
31	93.15	?			
32	93.82	?			
33	94.90	?			
34	100.48	C13	Alcane	Tridecane	Confirme par standard
35	106.24	?			
36	106.52	?			
37	106.97	?			
38	107.93	?			
39	110.19	C14	Alcane	Tetradecane	Confirme par standard
40	113.06	?			
41	114.08	?			
42	115.49	C15	Alcane	Pentadecane	Confirme par standard
43	117.46	?			
44	119.38	C16	Alcane	Hexadecane	Confirme par standard
45	120.91	?			
46	122.49	C17	Alcane	Pentadecane	Confirme par standard
36	125.08	C18	Alcane	Octadecane	Confirme par standard
39	127.62	C19	Alcane	Nonadecane	Confirme par standard

3.2.3.4 Test no 2 (ZKQ-IB4A-0.4% Na) and Test no 3 (Co-ZKQ-IB4A-(0.4% Na+5% La)

The catalyst used in Test no 2 was prepared by impregnating the base zeolite with an amount of Na equivalent to 0.4% by weight of the catalyst by the wet incipient technique. The catalyst used in Test no 3 was prepared by exchanging the same base zeolite with cobalt followed by impregnation with 0.4 wt% Na and 5% by weight of La. The results of these two tests are presented int Tables A3 and A4 respectively.

In light of these results and those of Test no 1 in which the unmodified base zeolite was tested, the following conclusions can be drawn:

- Compared to the results of Test no 1 which was conducted at 310°C instead of 300°C, one can note an increase in both CO conversion and CO_2 selectivity in Tests no 2 and 3 with the latter registering the highest increase. This seems to indicate that at least part of this increase is attributable to the presence of sodium. In other words, sodium appears to enhance the shift reaction.

- As expected, methane selectivity was lower in Test no 2 than in Test no 1 on account of higher Na content; alkali metals are known to depress methanation.

- The higher total hydrocarbon selectivity in Test no 3 appears to be due to the presence of La and/or Co. Exchanged Co did not suppress the internal shift reaction, most probably because of its rather low concentration in the catalyst.

- The higher paraffin (36.60% vs 29.58%) and the lower olefin (48.52% vs 52.75%) contents in the liquid hydrocarbons derived from Test no 3 are most probably attributed to the presence of cobalt which is known to be a good hydrogenating metal.

- The presence of Co and probably of La appears to reduce aromatics production.

- The fact that an extremely long induction time of 192 h was needed before the appearance and thereafter the progressive build-up of $C_{13}+$ hydrocarbons in the organic phase in both Tests no 2 and 3 can only suggest that impregnated sodium by the wet incipient technique does not enhance sufficiently the production of distillate range products. This leads us to believe that impregnation did not instantly cause the sodium to enter the pore channels of the zeolite and replace H^+ ions. In sum, then, we may conclude that the primary role of sodium would be to neutralize the acid sites of the zeolite and any excess thereof is directed towards promoting the production of higher molecular weight products particularly those in the distillate range. It is noteworthy that previous studies have shown that ZKQ-IB catalysts in the acid form do produce only gasoline range hydrocarbons.

In light of the above, it is therefore vital that the incorporation of sodium to the base zeolite be effected not by impregnation but rather by ion exchange followed by evaporation of the entire solution in order to ensure not only the neutralisation of the acid sites but also the quantitative uniform dispersion of the added sodium in the catalyst.

3.2.3.5 Test no 4 (0.4% Na-ZKQ-IB4A) and Test no 5 (0.67% Na-ZKQ-IB4A)

Both catalysts were prepared by exchanging the base zeolite with an aqueous sodium nitrate solution of the required strength at 90°C followed by evaporation of the entire solution and calcination at 500°C. The results of these two tests are presented in Tables A5 and A6 respectively.

Evidence that the method used in incorporating sodium in the catalysts profoundly influences product distribution is clearly demonstrated by a comparison of the results of Test no 2 and 4 of catalysts containing the same amount of sodium which has been incorporated in two different ways as detailed above.

The two catalysts behaved differently in the following respects:

- C_1 and C_2 hydrocarbon selectivities at 240 hours on stream were as expected lower for Test no 4 than for Test no 2 (20.49% vs 23.26% for C_1 and 10.95% vs 12.87% for C_2). This is probably attributable to the neutralization of the Bronsted acid sites by the exchanged sodium.

- Although the overall conversions of CO and H_2 were about the same in both cases, substantially more paraffins (42.03% vs 28.36%), significantly less olefins (43.31% vs 54.95%) and less aromatics (6.61% vs 8.59%) were produced at 240 hours on stream in Test no 4 than in Test no 2.

- Furthermore, C_{5+} hydrocarbons selectivity was significantly higher in Test no 4 than in Test no 2 (35.80% vs 27.64%).

- Selectivity to C_{13}-C_{22} distillate fraction was substantially higher in Test no 4 than in Test no 2. Moreover, a comparison of the simulated distillation curves shows that the fraction of heavier hydrocarbons produced in Test no 4 was higher than that produced in Test no 2.

These results seem to support the view that in order to improve C_5+-hydrocarbons selectivity and promote the production of distillate range products it is necessary to carry out sodium exchange followed by evaporation of the entire solution before final calcination of the sodium-exchanged base zeolite.

The effect of increasing the amount of added sodium to the base zeolite are brought to light when the results of Test no 4 and 5 are compared. They differ from each other in the following respects:

- Although the overall syngas conversions for 0.4% Na-ZKQ-IB4A in Test no 4 was higher than that of 0.67%Na-ZKQ-IB4A in Test no 5, total hydrocarbons selectivities were virtually the same for both catalysts at 336 ours on stream (16.71% vs 16.80%).

- C_1-C_4 selectivity was consistently higher for 0.67% Na-ZKQ-IB4A than for 0.4% Na-ZKQ-IB4A.

- PONA analyses of the liquid hydrocarbons sampled at 336 hours on stream show that 0.4% Na-ZKQ-IB4A yielded substantially more paraffins (45.38% vs 32.58%) and aromatics (11.19% vs 6.60%) and sunstantially less olefins (40.05% vs 47.25%) than 0.67% ZKQ-IB4A.

- The chromatograms of the liquid hydrocarbons derived from the two tests showed stronger C_{13}-C_{20} hydrocarbons peak intensities for 0.4% Na-ZKQ-IB4A than for 0.67% Na-ZKQ-IB4A.

In light of the foregoing, it appears that virtually all the remarks made contradict in some way what was earlier said about the influence of Na on C_{5+} hydrocarbons selectivity and product distribution. There seems to be a number of possible reasons that could explain these apparent anomalies.

Alkalisation of iron catalysts have been shown to affect chain length, chain branching, ratio of olefins to paraffins, alcohol, carbon and methane selectivity (54). In reference in particular a whole chapter of the book is devoted to the effect of alkalisation of iron catalysts. For instance, methane selectivity reaches a minimum value with increasing alkali metal doping before showing an increase with more added alkali metal. Increasing alkali metal doping also promotes deposition of carbon. Therefore, our data seem to suggest that there is an optimum concentration of Na which can be incorporated in the catalyst to maximise C_{5+} hydrocarbons production particularly that of straight chain saturates in the distillate range at the expense of light hydrocarbons production. Our data equally seem to suggest that the optimum Na concentration lies below 0.67 wt%. Secondly, as expected, carbon deposition (0.25 g vs 0.2 g C/100 g CO) and light hydrocarbons were higher on 0.67% Na-ZKQ-IB4A than on 0.4% Na-ZKQ-IB4A.

We believe that the above observations still hold despite the fact that the material balance in Test no 4 is low.

3.2.3.6 Test no 8 (0.4% Na-ZKQ-IB4A)

This test was carried out in order to find out whether or not the use of a binder/lubricant such as Sterotex admixed with the catalyst to facilitate pelletization thereof would have any effect on the activity and selectivity of the catalyst. The catalyst was therefore mixed with 4.76% by weight of Sterotex (stearic acid) and the mixture was pelletized. Thereafter the pellets were calcined in air at 500°C for 4 hours to remove the lubricant.

Comparing the results of this test shown in Table A9 with those of Test no 4 in which the catalyst tested was pelletized without Sterotex, we find that both catalysts behaved differently in the following respects:

- CO conversion was slightly lower in Test no 8 (74% vs 77%) and the H_2 conversions in both tests were the same.

- C_5+-hydrocarbons selectivity was substantially higher in Test no 4 than in Test no 8 (5.38% vs 2.65%) and $(C_1\text{-}C_4)/C_{5+}$ selectivity of Test no 8 was more than twice higher than that of Test no 4.

- The results of PONA analyses of the liquid hydrocarbons collected from both tests indicate that the catalyst pelletized with Sterotex yielded a product which had substantially lower paraffins content (31% vs 45%), significantly higher contents in olefins (47% vs 40%), naphtenes (11% vs 8%) and aromatics (10.5% vs 6.6%).

On the basis of these results, it is to be concluded that the use of Sterotex as a lubricant is detrimental to catalytic activity and selectivity. This may probably be attributed to two factors which involves carbon: first, it is possible that the temperature and the duration of calcination were not high enough to drive off all carbon residues from the catalyst which would therefore negatively affect catalytic activity. Secondly, during calcination some iron oxide could have reacted with the Sterotex to form iron stearate which upon decomposition would lead to the formation of inactive ferrocarbon materials of indefinite compositions.

3.2.3.7 Test no 9 (0.4% Na-ZKQ-IB4A) - effect of preoxidation

As stated in the first part of this chapter, previous studies have shown that preoxidised supported iron catalysts are easier to reduce and in some cases would have activities far greater than those demonstrated by the same pre-reduced catalysts. ZKQ-IB4A catalysts can be considered as iron supported zeolite catalysts and as such should benefit from a pretreatment involving oxidation in a current of a gaseous mixture comprising 50% oxygen and 50% helium, which is used to moderate the exothermic reaction and as a heat sink since it is a good heat conductor.

The pretreatment procedures employed in this test were given section 3.2.1. The preoxidised catalyst was then tested under the synthesis conditions outlined in Table A10 which also gives the results of the test.

After 112 hours on stream the preoxidised catalyst did not show any activity in terms of hydrocarbon formation. It was therefore reduced in flowing hydrogen (GHSV = 1000 h^{-1}) at 400°C for 24 hours. Thereafter, it was operated under synthesis conditions.

The following comments can be made on the basis of a comparison of the results of this test with those of Test no 4 in which the same catalyst was not subjected to a preoxidation step.

- Preoxidation of the catalyst followed by reduction in flowing hydrogen seems to increase synthesis gas conversion (77.74% vs 73.56% at 240 hours on stream).

- No meaningful conclusion can be drawn in regard to total hydrocarbon and CO_2 selectivity on account of the fact that the material balance was extremely poor.

- However, in regard to the nature of the liquid products, we find that the liquid hydrocarbons produced in Test no 9 was definitely more olefinic, aromatic and naphtenic and less paraffinic than those produced in Test no 4. The fact that no catalytic activity was observed with the preoxidised catalyst can only mean that ferric oxide (orange red colour) was not converted quickly enough to magnetite in flowing synthesis gas over a period of 112 hours. But once reduced in flowing hydrogen, the activity of the catalyst in terms of syngas conversion was indeed higher than that encountered in Test no 4. Aside from this remark no definite conclusion can be drawn in regard to selectivity because of the poor material balance of this test.

3.2.3.8 Test no 10 (ZKQ-IB4A-0.3% Ru) and Test no 11 (ZKQ-IB4A-0.5% Ru)

Ruthenium which is known to be the most active F-T metal is however inactive in regard to the water gas shift reaction (39). Water is usually the principal oxygen-containing product.

Tables A11 and A12 show the results of Tests no 10 and 11 which were conducted at two pressures, namely 1020 and 2720 kPa. Synthesis gas conversions for the catalysts impregnated with 0.3 and 0.5% Ru at 288 hours on stream were 58.38 and 78.83% with the corresponding total hydrocarbons selectivities of 12.54 and 17.24%. These results indicate that the 0.5% Ru catalyst is more active than the 0.3% Ru catalyst. In both cases light hydrocarbons selectivities were higher than that in Test no 4. An overall increase in syngas conversions and in water and total hydrocarbons selectivities and a decrease in methanation were observed when the reaction pressure was increased to 2720 kPa.

The catalyst with the higher Ru content yielded substantially more CO_2 than the one with lower Ru content (50.18% vs 32.75% at 384 hours on stream and 2720 kPa pressure). Furthermore, liquid hydrocarbons selectivity increased from 3.25% to 4.76% and from 1.75% to 3.69% with respect to total feed for the catalysts impregnated with 0.5% and 0.3% Ru respectively. The liquid hydrocarbons produced over the 0.5% supported Ru catalyst had a higher paraffins content (40.86% vs 35.57% at 1020 kPa and 47.11% vs 39.90% at 2070 kPa) and a lower naphtenes content (9.19% vs 12.40% and 6.76% vs 10.30%) than those of the 0.3% supported Ru catalyst. In both cases, the olefins and aromatics contents were comparable. The 0.5% supported Ru catalyst produced more distillate than the other catalyst. On the basis of the above results and of a comparison of these results with those of Test no 4 in which the same catalyst without impreg-

nated Ru was used, it may be concluded that the modification of ZKQ-IB4A catalyst by impregnation with Ru does not appear to improve liquid hydrocarbon selectivity but in actual fact decreases it (C_{5+}/total HC was 36.15% in Test no 4 and 27.74 and 30.48% in Tests no 10 and 11).

3.2.3.9 Test no 13 (Zn-ZKQ-IB4A (La))

The catalyst used in this test was prepared by exchanging the base zeolite with zinc followed by impregnation with 5% by weight of La. No sodium was added to the catalyst. The incorporation of zinc in zeolite of the ZSM-5 type is known to promote aromatisation. Coupled with La which we think enhances linear paraffins and/or alcohol production, this catalyst was expected to maximise liquid hydrocarbon yield with higher aromatic content.

From an examination of the results showns in Table A14 the following observations can be made:

- As expected at 167 hours on stream synthesis gas conversion reached 82.0% to give a total hydrocarbon selectivity of 17.65%.

- C_{5+}-hydrocarbons constituted 40.30% of the total hydrocarbons.

- High octane gasoline constituted about 90% of the liquid hydrocarbons, with the remaining 10% boiling in the diesel range.

- As expected, the presence of zinc was responsible for the increase in the aromatic content of the liquid hydrocarbons which was 28.44%.

- CO_2 selectivity was however quite high, reaching 57.40% at 167 hours on stream.

In conclusion, we believe that by doping the catalyst with Na, it would be possible to increase the co-production of diesel while maintaining the quality of the gasoline.

3.2.3.10 Olefinicity and isomericity of reactions catalysed by ZKQ-IB4A based catalysts

Defined as the ratio of olefins/total hydrocarbons of the same carbon number, the olefinicity of each of the various zeolites was determined with respect to C_2 to C_4 hydrocarbons only. Isomericity was defined in same way but only for C_4 hydrocarbons. In calculating these values from the GC data of the gas phase, no attempt was made to include the small and negligible amounts of light hydrocarbons which had dissolved in the liquid hydrocarbon phase.

The calculated values for the olefinicity and isomericity of each test are presented in Table 10. An examination of the data obtained for Tests no 2, 4, 5 and 9 enables us to make the following observations:

- Except for the olefinicity of Test no 4, which increased to a miximum and then decreased as a function of time, the olefinicity increased whereas the isomericity decreased with time on stream in all the other tests.

- Compared to those of Tests no 2, 5 and 9, Test no 4 had the lowest olefinicity.

Co, Na-exchanged and La-impregnated catalysts altered the olefinicity and isomericity of the reactions by lowering them. From the results of Tests no 3, 6 and 7 we can deduce the following points:

- In all three tests olefinicity increased as a function of time.

- Compared to that of Test no 2, C_{2+} olefinicity was substantially reduced in all the three tests. This is attributed to the presence of cobalt which would tend to hydrogenate the ethylene produced.

- C_3 and C_4 olefinicities were also reduced but to a lesser degree than C_2 olefinicity.

- Isomericity decreased with time in Tests no 3 and 7 but increased in no 6.

- Test no 7 displayed no isomericity at 144 hours on stream and thereafter; in point of fact, it had the lowest isomericity among all the tests. This lack of isomericity is highly desirable when the objective is to maximise the production of high quality diesel fuel.

- When the incorporation of Na was carried out by impregnation using the wet incipient technique as was the case in Test no 3, olefinicity is generally less than those of Tests no 6 and 7. We shall recall that the procedures employed to add sodium to the catalysts used in these two tests involved Na exchange

followed by evaporation of the entre solution prior to calcination thereof.

The effect of using stearic acid as a lubricant to facilitate pelletization of the catalyst on olefinicity and isomericity is best illustrated by comparing the results of Test no 4 wherein the catalyst used was pelletized without lubricant and of Test no 8 whose catalyst was admixed with lubricant prior to pelletization. The use of lubricant generally reduce C_2 and C_3 olefinicities but slightly increased that of C_4. However, it did not affect isomericity. Had there been a change in the surface acidity of the catalyst following the decomposition of the lubricant during calcination, this would have been reflected in a significant change in isomericity. Possible reasons for the reduction in olefinicity are:

- The iron oxide of the catalyst could have partially reacted with the lubricant or the carbon arising from the latter's decomposition. Iron is known to produce olefins.

- There could have been a redistribution of sodium during calcination which would have lowered the surface Na concentration therby leading to a decrease in olefinicity. High surface Na concentration generally promotes olefins formation.

The two Ruthenium-impregnated ZKQ-IB4A catalysts used in Tests no 10 and 11 generally had substantially lower C_2 and C_3 olefinicities than those of Test no 4 in which the same Na-exchanged base catalyst was used. C_4 olefinicities however were only marginally lower than that of Test no 4.

TABLE 10: Olefinicity and isomericity of modified ZKQ-4A zeolites as a function of time on stream

TIME ON STREAM (h)	$C_2^=$ /TOT. C_2	$C_3^=$ /TOT. C_3	$C_4^=$ /TOT. C_4	ISO-C_4/TOT. C_4
CATALYST: ZKQ-4A-(.4Na); RUN 2				
48	36.09	60.55	84.50	3.10
96	39.75	71.65	88.06	1.49
144	41.28	74.83	88.73	1.41
192	40.78	76.43	89.21	1.44
240	41.34	77.91	88.49	1.44
288	41.21	78.95	84.72	0.69
336	41.53	79.66	88.73	0.70
CATALYST: Co-ZKQ-(.4Na + 5% La); RUN 3				
48	10.29	37.72	71.11	6.67
96	11.59	43.80	77.24	4.14
144	13.08	50.38	80.39	3.27
192	14.29	53.85	80.77	2.56
240	15.46	57.89	81.94	1.94
288	16.59	60.87	81.82	1.95
336	17.48	62.72	82.72	1.85
CATALYST: ZKQ-4A.4Na; RUN 4				
48	37.21	68.00	85.00	1.67
96	40.99	76.32	86.32	0.85
144	42.04	77.85	86.55	0.84
192	41.61	77.58	84.25	0.79
240	39.75	76.79	84.80	0.80
288	37.58	75.29	83.97	0.76
336	35.09	73.86	82.96	0.74
CATALYST: ZKQ-4A.67Na; RUN 5				
48	33.53	74.11	84.25	2.36
96	35.88	75.32	88.37	0.78
144	36.72	76.16	89.15	0.78
192	37.70	77.84	89.47	0.75
240	38.25	78.72	89.39	0.76
288	38.59	79.47	89.23	0.77
336	39.01	79.58	89.06	0.78

TABLE 10 (con'd): Olefinicity and isomericity of modified ZKQ-4A zeolites as a function of time on stream

TIME ON STREAM (h)	$C_2^=$ /TOT. C_2	$C_3^=$ /TOT. C_3	$C_4^=$ /TOT. C_4	ISO-C_4/TOT. C_4
CATALYST: Co-ZKQ-4A.4Na(La); RUN 6				
48	20.31	67.72	86.21	0.86
96	23.31	75.00	87.72	0.88
144	25.76	77.03	86.92	0.93
192	26.12	77.85	86.92	0.93
240	26.92	78.32	87.13	0.99
288	27.34	78.57	86.46	1.04
336	26.56	78.57	85.42	1.04
CATALYST: Co-ZKQ-4A.67Na(La): RUN 7				
48	16.78	68.03	81.44	1.03
96	17.24	70.34	80.22	1.10
144	23.31	75.17	84.62	0
192	24.59	76.12	83.91	0
240	25.22	76.38	84.34	0
288	25.00	75.81	83.95	0
336	24.07	75.59	83.53	0
CATALYST: ZKQ-4A.4Na + STEROTEX; RUN 8				
48	32.45	64.57	86.18	1.63
96	41.07	70.75	88.10	0.79
144	34.71	72.02	88.06	0.75
192	33.33	72.43	87.77	0.72
240	32.09	72.40	87.50	0.69
288	20.53	72.41	86.93	0.65
336	28.87	71.50	86.67	0.67
384	27.69	70.59	86.39	0.68
CATALYST: ZKQ-4A.4Na; RUN 9				
48	36,75	68.79	87.60	1.55
96	39.66	74.85	89.21	0.72
144	40.43	77.37	89.58	0.69
192	40.84	78.17	89.86	0.68
240	40.64	78.39	89.80	0.68

TABLE 10 (con'd): Olefinicity and isomericity of modified ZKQ-4A zeolites as a function of time on stream

TIME ON STREAM (h)	$C_2^=$ /TOT. C_2	$C_3^=$ /TOT. C_3	$C_4^=$ /TOT. C_4	ISO-C_4/TOT. C_4
CATALYST: ZKQ-4A.3Ru: RUN 10				
48	18.40	63.57	80.00	1.05
96	36.36	75.49	84.51	0
144	24.83	68.46	85.00	0.83
192	25.36	66.41	85.96	0.88
240	24.64	67.16	85.34	0.86
288	24.64	68.38	85.59	0.85
336	21.57	68.60	78.98	1.70
384	17.89	71.06	79.09	1.31
CATALYST: ZKQ-4A.5Ru; RUN 11				
48	33.66	69.90	85.30	1.12
96	18.49	67.13	76.53	0
144	6.67	48.53	74.12	1.18
192	8.30	53.94	78.05	0.61
240	9.22	58.06	79.63	0.62
288	9.81	59.76	80.50	0.63
336	8.18	59.93	77.01	1.07
384	7.58	60.80	76.19	1.06
CATALYST: Zn-ZKQ-4A (La): RUN 13				
47	22.02	38.10	77.42	22.58
95	17.45	34.52	54.62	22.69
167	13.83	31.96	54.96	21.37

The catalysts with lower Ru content (0.3 wt%) gave rise to higher C_2, C_3 and C_4 olefinicities than the one with higher Ru content (0.5 wt%). This appears to be due to the hydrogenation property of Ru.

In regard to isomericity, it appears that the ruthenium supported catalysts only slightly promotes isomerisation when compared with the corresponding result of Test no 4.

Finally, as expected, the Zn-exchanged and La-impregnated base zeolite, Zn-ZKQ-IB4A (La) gave rise to low C_2, C_3 and C_4 olefinicities and to the highest isomericity among all of the tests. This is attributed to the fact that no sodium was added to the catalyst to neutralize its acid sites, which generally favour isomerisation and aromatisation. The presence of zinc equally is conducive to aromatization of olefins. It is therefore not surprising that the liquid hydrocarbons formed over this catalyst had the highest aromatics content as well as the highest content in branched paraffins.

In light of the above results, we can conclude that: sodium would generally give rise to high olefinicity and low isomericity. Impregnated sodium, that is surface sodium, leads to higher olefinicity than exchanged sodium.

- Being a good hydrogenating metal, cobalt definitely decreases olefinicity; the same remark applies to ruthenium whose hydrogenating power is apparently greater than that of cobalt in view of the lower olefinicity encountered with it.

- Exchanged zinc substantially lowers olefinicity, increases isomericity and promotes aromatisation such that it should be used to promote the production of high octane gasoline. In

point of fact high octane gasoline constituted 90% by volume of the liquid hydrocarbons produced over the zinc-exchanged catalyst.

3.2.3.11 Simulated distillation of product liquid hydrocarbons

The results of simulated distillation (ASTM D-2887) of product liquid hydrocarbons derived from each of the tests and from the tests performed at Queens University are reported in the corresponding table in Appendix A, summarised in Table 11, and plotted in Figures 14 to 16. From Figures 13 and 14 the fractions of gasoline, diesel and wax constituting the product liquid hydrocarbons have been computed and they are presented in Table 12. Likewise, the calculated values obtained for the samples from Queens University are shown in Table 13.

As seen in Table 12, Test no 7 yielded the highest amount of diesel followed by Tests no 11 and 10 in which the Ru-impregnated catalysts were tested. The catalysts used in Test no 7 was Co, 0.67%Na-ZKQ-IB4A (La). The zinc-exchanged and La-impregnated catalyst produced the highest quantity of gasoline range product which contained the highest aromatics and the lowest paraffinic contents. As mentioned earlier, in attempting to maximise diesel production it is important to incorporate sodium in the catalyst and avoid altogether the use of zinc.

According to the results shown in Table 13, sample no 4 which was collected almost at the end of the test showed a split of 22% gasoline and 73.0% diesel. The other samples were collected at 1, 2 and 3 weeks on stream.

TABLE 11: Summary of hydrocarbons compositions and simulated distillation

RAPPORT	GAZ	DE	SYNTHESE									
DATE	10-Dec-86	10-Dec-86	03-Feb-87	03-Feb-87	20-Mar-87	20-Mar-87	24-May-87	26-May-87	17-Jun-87	17-Jun-87	02-Oct-87	02-Oct-87
CATALYSEUR	ZrO2-M-(Na)	Co-ZrO2-(Na+SiO2La)	ZrO2-M-.3Na	ZrO2-M-.5Na	Co-ZrO2-M-.3Na(La)	Co-ZrO2-M-.5Na(La)	ZrO2-M-.3Na	ZrO2-M-.5Na	ZrO2-M.5Na	ZrO2-M.5Na	Co-ZrO2-M-.5Na(La)	Zn-ZrO2-M(La)
ESSAI #	2	3	4	5	6	7	BCS(FORMIC ACID)	9A	10	11	12	13
# HEURES D'ESSAI	336	336	336	336	336	336	384	240	384	384	167	167
P O N A (%v)												
P / HC CLIQ	29.58	36.60	45.30	52.58	35.37	43.55	30.82	31.98	39.98	47.11	45.71	20.46
O / HC CLIQ	52.75	48.52	40.05	47.25	42.95	36.97	47.75	48.02	39.23	36.38	30.68	31.88
A / HC CLIQ	0.18	0.52	7.97	0.98	10.17	8.52	10.89	10.53	10.38	6.76	8.54	11.38
N / HC CLIQ	9.57	6.37	6.68	11.19	11.50	8.56	10.54	9.47	10.57	9.75	15.07	20.44
C1/HC TOTAUX	31.86	23.51	20.83	23.57	23.31	19.55	23.85	20.41	24.34	20.96	20.97	25.19
C2/HC TOTAUX	11.84	12.00	10.72	13.00	10.55	9.08	13.33	11.76	12.32	12.16	11.65	11.16
C3/HC TOTAUX	16.70	14.28	16.03	19.72	16.62	15.30	20.19	18.13	19.12	19.90	10.51	8.45
C4/HC TOTAUX	17.77	17.91	16.27	17.62	14.97	13.45	19.20	17.69	16.48	16.51	15.75	14.90
C5+/HC TOTAUX	31.83	32.31	36.15	26.09	34.50	42.62	23.35	32.00	27.74	30.48	33.11	40.30
DISTILLATION SIMULEE ASTM D2887												DIESEL
% OFF (C)												
IBP	85	67	29	33	26	36	26	32	31	30	43	25	124
10	116	100	99	95	93	98	86	92	90	94	119	88	190
20	127	110	114	114	113	124	107	112	121	120	142	109	222
30	142	120	127	126	125	147	120	129	143	142	157	121	242
50	166	156	164	159	162	187	148	159	178	174	180	142	278
70	196	192	206	199	203	238	180	199	221	219	227	163	311
80	216	215	230	221	233	276	202	220	255	254	250	178	329
90	254	253	286	272	289	335	237	279	307	302	299	199	351
FBP	361	391	414	416	436	459	355	419	446	409	386	311	405

SIMULATED DISTILLATION PROFILE

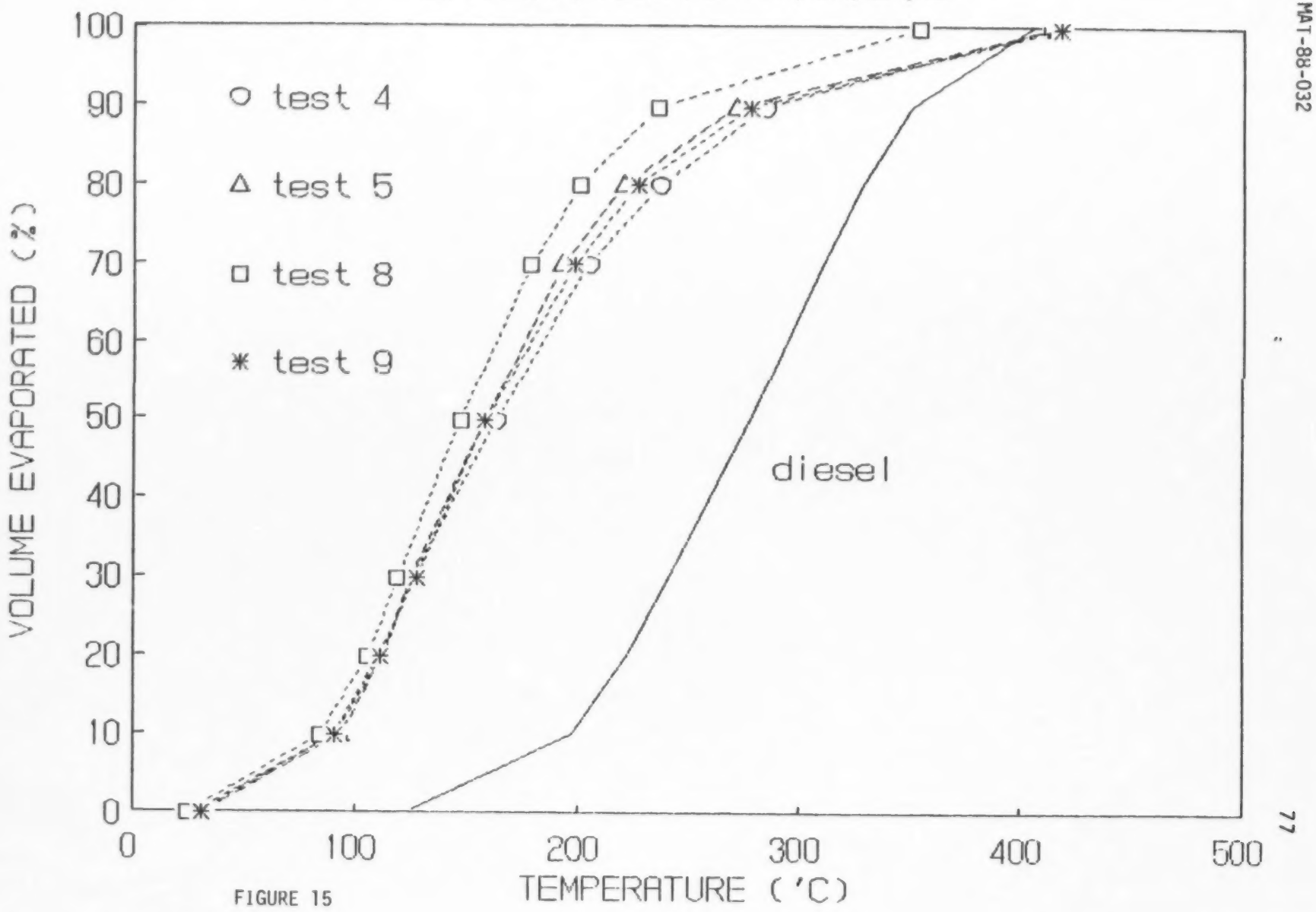


FIGURE 15

MAT-88-032

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SIMULATED DISTILLATION PROFILE

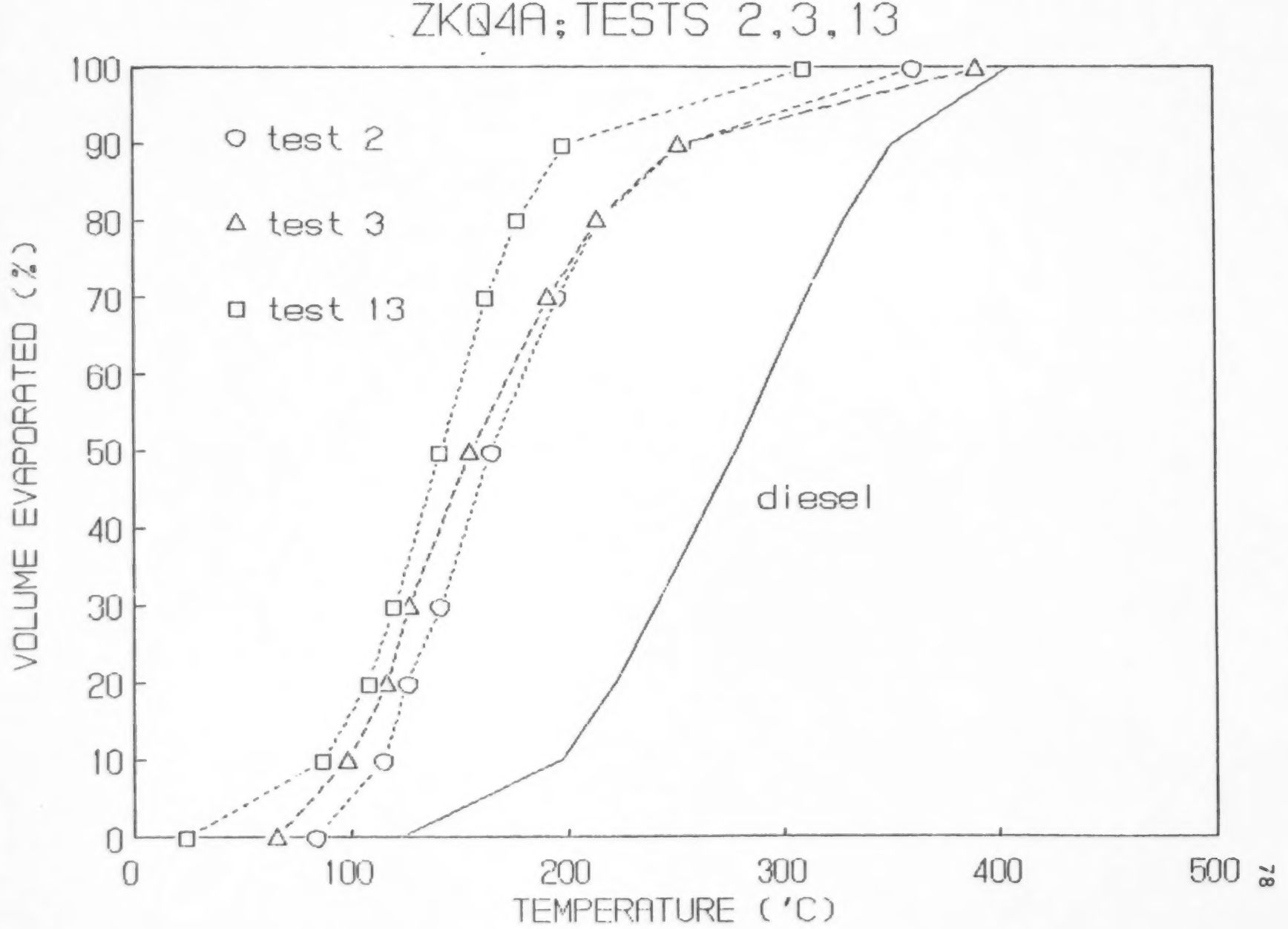

FIGURE 16

TABLE 12: Simulated distillation of product liquid hydrocarbons (fixed bed reactor)

B.P. RANGE	TESTS											COMMERCIAL DIESEL
	NO 2	NO 3	NO 4	NO 5	NO 6	NO 7	NO 8	NO 9	NO 10	NO 11	NO 13	
V% 0 to 200°C (gasoline)	74.0	73.0	68.0	72.5	70.0	57.0	78.0	70.0	62.0	63.5	90.0	11.0
V% 200°C-405°C (diesel)	26.0	27.0	31.0	26.5	28.0	40.0	22.0	29.0	35.0	36.50	10.0	89.0
V% 405°C plus ("wax")	0.0	0.0	1.0	1.0	2.0	3.0	0.0	1.0	3.0	0.0	0.0	0.0
G/D*	2.85	2.70	2.19	2.74	2.50	1.43	3.55	2.41	1.77	1.74	9.0	0.12

* Gasoline to diesel ratio

TABLE 13: Simulated distillation of samples from Queens University (modified Berty reactor)

B.P. RANGE	SAMPLES				COMMERCIAL DIESEL
	NO 1	NO 2	NO 3	NO 4	
V% 0 to 200°C (gasoline)	44.0	47.0	50.0	22.0	8.0
V% 200-405°C (diesel)	54.0	49.0	48.0	73.0	92.0
V% 405°C plus ("wax")	2.0	4.0	2.0	5.0	0.0
G/D	0.81	0.96	1.04	0.30	0.09

3.2.3.12 Analyses of aqueous phase

Samples of the aqueous phase from Tests no 4 and 7 were analysed by GC/FTIR for their contents in oxygenates. Owing to the rather low sensitivity of FTIR compounded with the low concentration of some components, difficulties were encountered in regard to the low signal to noise ratio. The results were therefore inconclusive. Gas chromatographic analyses on Carbowax column using FID detector yield the results presented in Table 14. Methanol, ethanol and n-propanol were present in significant amounts in the aqueous phase of Test no 7 whereas in Test no 4 only methanol and ethanol were the main alcohols present in the aqueous phase. Acetone in minor amounts (ca 200 ppm in Test no 4 and 385 ppm in Test no 7) was the only ketone detected.

On the basis of these results we can conclude that:

- Either Co or La or both promote the production of simple alcohols and acetone.

- Both catalysts did not possess the required acidity to convert these oxygenates into hydrocarbons.

- Oxygenates constituted about 0.8% and 2% by weight of the aqueous phases of Tests no 4 and 7 respectively.

TABLE 14: GC analyses of aqueous phase

COMPONENTS	TEST NO 4 (ppm)	TEST NO 7 (ppm)
Acetone	199.9	385.3
Methanol	4396.9	6712.0
t-butanol	---	417.7
i-propanol	90.3	213.9
Ethanol	2589.0	9248.9
n-butanol	21.4	47.3
n-propanol	152.9	2811.0
i-butanol	2.7	115.1
3-pentanol	1.8	4.9
2-pentanol	5.8	18.1
pentanol	5.0	211.8

3.2.3.13 Determination of total carbon in used catalysts

Carbon may exist as free, carbidic, graphitic and carbonate carbons in used F-T iron catalysts. The determination of total carbon in the used catalysts can give us an idea of the susceptibility of each catalyst to «coking». All used catalysed were first ground thoroughly to a fine homogeneous powder and then analysed for their respective total carbon contents by combustion in a Leco furnace equipped with infrared detector. Visual examination of the used catalysts did not reveal any significant carbon build up.

The results of total carbon analysis are reported in Table 15. As expected, 0.67%Na-ZKQ-IB4A was found to have the highest coking susceptibility among all the catalysts. This is attributed to the fact that the rate of free and carbidic carbon formation increases with increasing alkali content. This catalyst had the highest Na content. Free carbon formation is also enhanced by using synthesis gas rich in CO. As seen in Table 15, the results indicate that there is a trend, albeit slight, towards less carbon formation when the Na-exchanged base catalysts are modified by the incorporation of Co and La or Ru. A significant reduction in carbon formation was observed with the catalyst admixed with Sterotex before pelletization. On the other hand, the Zinc-exchanged catalyst showed relatively moderate carbon forming susceptibility on account of its higher cracking and aromatisation capabilities which are attributable to its higher acidity. It is noteworthy that «coke» formation which is a shape-selective process mainly originates from severe dehydrogenation of aromatic and fused aromatic compounds. However, it is restricted to the external surface of the catalyst only since no carbon deposit can form in the channels of the catalyst because of geometric restriction.

TABLE 15: Carbon deposit on used catalysts

CATALYSTS	RUN NO	wt% C	GRAM OF C/100 g CO
ZKQ4A(X3.5)	1	-	-
ZKQ4A(.4Na)	2	13.7	0.21
Co-ZKQ4A-(.4Na+5%La)	3	11.6	0.20
ZKQ4A-.4Na	4	13.4	0.20
ZKQ4A-.67Na	5	16.6	0.25
Co-ZKQ4A-.4Na(La)	6	11.8	0.19
Co-ZKQ4A-.67Na(La)	7	12.1	0.16
ZKQ4A-.4Na+Sterotex	8	14.8	0.15
ZKQ4A-.4Na	9	13.8	0.21
ZKQ4A-.3Ru	10	13.2	0.19
ZKQ4A-.5Ru	11	11.4	0.15
Co-ZKQ4A-.67Na(La)	12	7.9	0.21
ZN-ZKQ4A(La)	13	7.4	0.21

3.2.3.14 Typical composition of gasoline samples

We report in Table 16 the detailed compositions of gasoline samples of Tests no 2, 5, 7, 11 and 13. These results indicated quite clearly that the catalysts which have been modified only with Na (Tests no 2 and no 3) are better olefins producers than those which contain other metals. Olefins content appears to reach a maximum at C_7 or C_8 and then gradually tails off at C_{11}. These olefins as well as the light C_2 to C_4 olefins could be oligomerised to distillate range hydrocarbons over a pentasil zeolite of low acidity at high pressures and relatively low temperatures. This would increase the overall distillate yield.

The Co, Na-exchanged and La-impregnated base zeolite tested in Test no 7 produced the highest yield of straight chain paraffins whereas the Zn-exchanged and La-impregnated zeolite used in Test no 13 produced the least n-paraffins but the highest yield of aromatics. The catalyst in Test no 7 is therefore regarded as a diesel-producing catalyst whereas that in Test no 13 is considered to be a gasoline-producing catalyst.

TABLE 16: Typical compositions of gasoline samples taken at 192 hours on stream

CATALYST	ZKQ-4A(.4Na)	ZKQ-4A.67Na	Co-ZKQ-4A.67Na(La)	ZKQ-4A.5Ru	Zn-ZKQ-4A(La)
RUN NO	2	5	7	11	13*
			wt%		
C_5					
n-pentane	0.365	0.313	0.398	0.486	0.453
i-pentane	0.092	---	---	---	0.434
C_5-olefins	4.888	3.454	2.133	2.304	2.107
Total C_5	5.345	3.767	2.531	2.790	2.994
C_6					
n-hexane	0.835	0.818	1.293	1.301	0.893
methyl-pentane	0.385	0.276	---	0.116	1.267
methyl cyclo-pentane	---	---	---	---	0.156
C_6-olefins	8.900	8.640	5.780	5.590	3.310
Total C_6	10.120	9.734	7.073	7.007	5.626
C_7					
n-heptane	1.379	1.496	3.000	2.342	0.995
branched C_7-P	2.182	1.635	0.554	1.397	2.922
dimethyl cyclo-C_5	---	---	---	---	0.466
ethyl cyclo-C_5	---	---	---	---	0.143
methyl cyclo-C_6	---	---	---	---	0.285
C_7-olefins	15.680	15.270	11.490	10.200	6.090
Total C_7	12.241	18.401	15.044	13.939	10.901
C_8					
n-octane	3.443	3.851	5.905	4.936	1.757
branched C_8-P	2.822	2.381	1.559	2.811	5.122
C_8-olefins	11.990	12.420	6.590	9.460	8.810
C_8-naphtenes	2.540	2.490	4.740	2.050	3.220
Total C_8	20.795	21.142	18.794	19.257	18.909
C_9					
n-nonane	1.735	2.194	5.700	4.135	0.794
branched C_9-P	4.826	4.716	4.097	3.024	4.873
C_9-olefins	7.512	7.781	7.190	6.527	7.954
C_9-naphtenes	3.753	4.702	2.970	6.692	5.120
Total C_9	17.829	19.393	19.957	20.378	18.741

TABLE 16: Typical compositions of gasoline samples taken at 192 hours on stream (continuation)

CATALYST	ZKQ-4A(.4Na)	ZKQ-4A.67Na	Co-ZKQ-4A.67Na(La)	ZKQ-4A.5Ru	Zn-ZKQ-4A(La)
RUN NO	2	5	7	11	13*
			wt%		
C_{10}					
n-decane	1.407	1.593	4.385	3.110	0.681
branched C_{10}-P	4.339	4.683	3.893	5.622	4.589
C_{10}-olefins	2.501	2.908	2.751	1.964	2.389
C_{10}-naphtenes	2.342	1.877	2.085	1.780	1.911
Total C_{10}	10.589	11.061	13.114	13.476	9.570
C_{11}					
n-undecane	1.391	1.696	5.491	3.643	0.394
branched-C_{11}-P	0.792	1.258	1.756	2.775	2.374
C_{11}-olefins	0.497	0.556	---	0.795	0.678
Total C_{11}	2.680	3.510	7.247	7.213	3.446
C_{12}					
n-dodecane	0.974	1.312	4.607	2.935	---
branched C_{12}-P	0.720	1.018	1.717	2.046	0.595
C_{12}-olefins	0.324	---	---	---	---
Total C_{12}	2.018	2.330	6.324	4.981	0.595
C_{13}					
C_{13}-olefins	---	---	---	0.751	---
Total C_{13}	---	---	---	0.751	---
AROMATICS					
A_6					
Benzene	0.421	0.346	---	0.180	0.403
A_7					
Toluene	0.604	0.599	---	0.296	0.727
A_8					
Ethyl benzene	0.386	0.427	---	0.251	0.424
o-xylene	0.699	0.912	0.202	0.151	0.426
m-xylene	0.845	0.260	---	0.658	3.133
p-xylene	0.289	0.265	0.239	1.275	
Total A_8	2.219	2.277	0.467	1.299	5.258

TABLE 16: Typical composition of gasoline samples taken at 192 hours on stream (continuation)

CATALYST	ZKQ-4A(.4Na)	ZKQ-4A.67Na	Co-ZKQ-4A.67Na(La)	ZKQ-4A.5Ru	Zn-ZKQ-4A(La)
RUN NO	2	5	7	11	13*
			wt%		
A_9					
o-ethyl toluene	0.390	0.470	---	---	---
m-ethyl toluene	1.061	0.516	1.074	0.794	5.424
p-ethyl toluene	---	---	---	---	4.945
trimethyl benzene (1, 2, 3)	---	---	---	0.101	---
trimethyl benzene (1, 2, 4)	0.210	0.271	0.568	0.281	2.034
trimethyl benzene (1, 3, 5)	0.536	0.573	0.357	0.633	0.331
n-propyl benzene	0.611	0.844	---	0.730	0.820
i-propyl benzene	0.200	0.242	0.577	0.229	0.084
C_9-aromatics (unidentified)	---	---	0.822	1.318	0.367
Total A_9	3.008	2.916	3.398	4.086	14.005
A_{10}					
tetramethyl benzene (1, 2, 4, 5)	0.197	---	---	---	0.383
n-butyl benzene	0.355	0.173	---	0.167	0.998
methyl propyl benzene	0.590	0.370	0.537	0.290	3.260
diethyl benzene	0.957	0.821	1.075	0.742	0.131
dimethyl ethyl benzene	---	0.194	0.300	---	0.757
C_{10}-aromatics (unidentified)	1.084	0.925	2.949	1.046	0.730
Total A_{10}	3.183	2.483	4.861	2.245	6.259
A_{11}					
methyl butyl benzene	---	---	---	0.217	---
C_{11}-aromatics (unidentified)	---	0.334	0.431	0.892	1.786
Total A_{11}	---	0.334	0.431	1.109	1.786

* Run 13 was taken at 167 hours-on-stream

3.2.3.15 Selection of the best catalyst for longer duration and scale-up test in modified Berty reactor of 200 ml capacity

Tables 11 and 16 give a summary of the hydrocarbons compositions and simulated distillation. On the basis of the results of all the tests save Test no 13, Co-0.67%Na-ZKQ-IB4A(La) was found to be the best all-round catalyst in terms of gasoline to diesel ratio, yield and quality of diesel, CO_2 selectivity, isomericity and carbon forming susceptibility. It was therefore selected for longer duration and scale-up tests in a 200 ml modified Berty reactor in the F-T catalysts testing laboratory at Queen's University. The Zn-exchanged catalyst tested in Test no 13 which was found to have the highest liquid hydrocarbons selectivity was not considered for the purpose of catalyst selection because of its very high selectivity to high octane gasoline. In fact it can be modified into a solely gasoline-producing catalyst.

The selected catalyst had a synthesis gas conversion of about 60 wt% which we consider to be moderate. Its CO_2 selectivity was below 37 wt% which is lower than that of the 0.67%Na-exchanged base catalyst (ca 50wt%). As seen in Table 12, Co-0.67%Na-ZKQ-IB4A (La) had the lowest gasoline to diesel ratio (1.43) and it yielded a liquid product which had the highest straight chain paraffins content and diesel fraction. As seen in Table 10, it had the lowest isomericity (zero isomericity) which is highly desirable in the production of high quality diesel. With the exception of the catalyst pelletized with Sterotex it displayed the lowest carbon forming ability which is conducive to the maintenance of long useful catalyst life.

Subsequent to the selection of the best performing catalyst, a 200 ml batch thereof was prepared and tested in our minireactor set-up before it was sent to Queens University in order to check whether the data obtained in Test no 7 could be reproduced. The results of this test (Test no 12) shown in Table A13 quite clearly indicate overall reduced syngas conversion, selectivities to total hydrocarbons, gaseous and liquid hydrocarbons when compared to those of run no 7. As seen in Table 3 which gives the results of elementary analysis of the catalyst, its lower Fe and Co contents might be a contributing factor to the catalyst's lower activity but this might be offset by the lower Na content which should increase syngas conversion. In regard to selectivity, the lower Na content should tend to lower the selectivity to high molecular weight hydrocarbons. Another contributing factor could be the relative degree of crystallinity of the catalyst. A low degree of crystallinity is not conducive to high catalytic activity.

3.2.3.16 Longer duration scale-up test in modified Berty reactor

The Co, Na-exchanged and La-impregnated catalyst was run for more than 4 weeks. Because of computer hardware problems which turned out to be virtually impossible to solve despite repeated efforts, there was no data on syngas conversion, selectivities etc. to enable the computation of mass balance. A GC chromatogram of organic liquid product is attached in appendix B. The report prepared in the form of a letter by Prof. B.W. Wojciechowski is included in Appendix C in its entirety.

4.0 CONCLUSIONS

The main objective of this project which is to maximise the production of distillate range hydrocarbons at the expense of gasoline has, in our view, been attained through the modification of ZKQ-IB4A base zeolite with metal such as Na, Co and La. Chromatographic analysis of the distillate range hydrocarbons has shown that they are composed mainly of highly desirable diesel range straight chain paraffins. Simulated distillation data have shown that very little wax is formed thereby demonstrating that the very presence of a zeolitic function in the catalyst serves to dampen more or less the rate of chain growth beyond the diesel range. The co-production of highly olefinic gasoline with aromatic content of about 9 wt% is significant in the sense that the straight chain olefins contained therein can be oligomerised to distillate range products at relatively high pressures and low temperatures over a pentasil zeolite of low acidity while the remaining hydrocarbons fraction would constitute a premium gasoline on account of the resulting relative increase in its aromatic content. This, therefore, constitutes a supplementary route to further maximise distillate production while simultaneously improving the octane rating of the co-produced gasoline and reducing its susceptibility to gum formation by removing the olefins. The olefinic distillate produced can be easily transformed into premium grade diesel by mild hydrogenation over a nickel catalyst.

On the basis of the results it has been shown that:

- Reduction of the catalyst in a current of a gas mixture comprising 75% H_2 and 25% He at 450°C and 1 atmosphere for 30 hours followed by carbiding at 325°C and 1 atm with synthesis gas having a H_2:CO ratio of 1:1 for 10 hours did inhibit heavy

coking that would have plugged the reactor or caused rapid inactivation of the catalyst. Indeed, all the catalysts still maintained their activities at the conclusion of the tests.

- Prior oxidation of the Na-exchanged base catalyst followed by testing of the oxidised catalyst under synthesis operating conditions inactivated the catalyst. Subsequent reduction of the catalyst in accordance with the procedures given above brought about a reactivation of the catalyst. It may therefore be concluded that prior oxidation of the catalyst does not appear to increase the activity of the catalyst but appears to inactivate it to the point where no hydrocarbons are produced. On the other hand, prior oxidation could have rendered the catalyst more amenable to reduction, thereby possibly giving rise to a more active catalyst.

- It appears that the optimum H_2:CO ratio of the feed gas is about 1 for maximising liquid hydrocarbons production. A ratio of 2 has been shown to produce hardly any liquid hydrocarbons over Co, 0.67%Na-ZKQ-IB4A(La).

- The sodium content of the catalyst as well as the method used in incorporating it therein have been found to exert a profound influence not only on synthesis gas conversion but also on hydrocarbons selectivity and on the composition of the liquid hydrocarbons. Beyond a certain optimum Na content, syngas conversion and selectivity to hydrocarbons decrease with increasing Na content. Furthermore, with increasing Na content, increase in olefinicity is generally accompanied by a drop in isomericity and aromacity. This is directly linked to a reduction in the acidity of the catalyst.

We have found that, for the purpose of reproducibility and to

maximise the effect of sodium, it is important that its incorporation into the catalyst be effected via ion exchange at or near the boiling point of water followed by evaporation to dryness of the entire solution rather than by impregnation using the wet incipient technique, which is not effective enough in bringing about complete neutralization of the acid sites. The extent of residual sodium removal from the base zeolite is definitely enhanced by the use of hot water for rinsing. The rate of formation of carbon whether in the elemental or combined state is enhanced by increases in sodium content.

- The use of Sterotex as a lubricant for facilitating pelletization of the catalyst tends to decrease the overall syngas conversion, total hydrocarbons and liquid hydrocarbons selectivities.

- Ru-impregnated base zeolite seems to produce lower yields of liquid hydrocarbons than the 0.4%Na-exchanged base zeolite. Its high CO_2 selectivity suggests that Ru enhanced the Bouduard reaction since it does not have any activity in regard to the shift reaction.

- Zn-exchanged and La-impregnated base zeolite has been shown to be a highly active high octane gasoline-producing catalyst. The relatively high aromatic content of the liquid product is attributable not only to zinc but also to the higher acidity of the catalyst to which no sodium was added.

- The Co, 0.67% Na-exchanged and La-impregnated catalyst was found to have the highest liquid hydrocarbon selectivity and the lowest gasoline to diesel ratio. The distillate range fraction containing mainly straight chain paraffins is there-

fore considered to constitute premium grade diesel in terms of cetane number and smoke. In short, this catalyst is diesel-producing. We believe that although the activity of the catalyst is moderate with a syngas conversion of about 60 wt% it can be further increased by incorporating into the catalyst the optimum amount of sodium and by increasing the operating pressure, which would equally favour the production of paraffins. The catalysts could be tailored in a way that would allow either the production high octane of gasoline only or that of premium grade diesel in order to meet shifts in demand. We can therefore consider this project and the previous one as ground work that could ultimately lead to the development of a process that would offer certain advantages over Mobil's MOGD process on account of the fact that the desired products are produced directly from syngas rich in CO rather than from methanol-derived or FCC-derived industrially important light olefins which is the case in the MOGD process.

5.0 RECOMMENDATIONS

In the absence of any major breakthrough in the direct conversion of natural gas to motor fuels or light olefins or for countries where coal or biomass is relatively cheap and abundant such that it can be gasified to synthesis gas, it is absolutely vital that work on F-T synthesis and related processes continues on. In light of the promising results obtained in this project it is recommended that further studies be done on the following research aspects:

- The optimisation of the iron and sodium contents of the catalyst for maximising diesel production.

- The optimisation of the zinc content for maximising the production of unleaded premium grade gasoline.

- To study the effect of various parameters such as pressure and temperature on syngas conversion and distillate range hydrocarbons selectivity.

- The oligomerisation of C_2 to C_7 olefins produced to distillate range products over ZKQ-IB catalysts of extremely low acidity in order to further increase diesel fuel yields.

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APPENDIX A

MATERIAL BALANCE, PRODUCT DISTRIBUTION
AND SIMULATED DISTILLATION
TABLES A1 - A14

TABLE A1

RAPPORT BAZ DE SYNTHESE		
DATE	20-Sep-86	22-Sep-86
CATALYSEUR	ZKQ1B4A(3.5)	ZKQ1B4A(3.5)
ESSAI #	1	1
# HEURES D'ESSAI	48	49
TEMPS D'ESSAI TOTAL	48	96
POIDS CATALYSEUR (g)	5.22	5.22
VOL. CATALYSEUR (ml)	8.00	8.00
GHSV (ml/h)/ml	300	300
PRESSION kPa	1020	1020
T1 (°C)	310	310
RATIO (H2/CO)	1.03	1.03
CONVERSION H2 (%wt)	54.61	61.60
CONVERSION CO (%wt)	50.28	62.39
PRODUITS (%wt)		
HC TOTAL / INPUT	8.91	11.72
HC (LIQ) / INPUT	1.26	3.04
HC (GAZ) / INPUT	7.65	8.68
EAU / INPUT	4.66	7.94
CO / INPUT	46.28	35.01
CO2 / INPUT	24.99	33.66
H2 / INPUT	3.14	2.65
BILAN MASSE (%wt)	87.98	90.99
SELECTIVITE:(C1-C4)/C5+	6.06	2.86
P O N A (%wt) *		
P / HC (LIQ)	33.42	33.42
O / HC (LIQ)	32.23	32.23
N / HC (LIQ)	11.38	11.38
A / HC (LIQ)	22.97	22.97
AROMATIZATION	3.26	5.95
C1/HC TOTAUX	28.19	25.36
C2/HC TOTAUX	14.39	13.29
C3/HC TOTAUX	12.59	10.64
C4/HC TOTAUX	22.93	18.69
C5+/HC TOTAUX	21.90	32.01

* Melange les deux vidanges pour injection

TABLE A2

RAPPORT GAZ DE SYNTHESE

DATE	3-10-85	3-12-85	3-14-85	3-16-85	3-18-85	3-20-85	3-22-85
CATALYSEUR	IB4A-16-10	IB4A-16-12	IB4A-16-14	IB4A-16-16	IB4A-16-18	IB4A-16-20	IB4A-16-22
ESSAI #	16	16	16	16	16	16	16
# HEURES CUM.	48	96	144	192	240	288	336
POIDS CATALYSEUR (g)	5.28	5.28	5.28	5.28	5.28	5.28	5.28
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	302	302	302	302	302	302	302
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020
T1 (°C)	310	310	310	310	310	310	310
CONVERSION H2 (%wt)	56.87	58.04	58.30	59.25	67.88	63.54	66.93
CONVERSION CO (%wt)	46.67	52.14	56.51	63.10	69.51	66.57	70.34
PRODUITS (%wt)							
HC TOTAL / INPUT	9.20	10.60	12.46	14.29	11.22	13.70	17.33
HC (LIQ) / INPUT	0.97	1.71	2.55	3.42	2.57	3.45	4.24
HC (GAZ) / INPUT	8.24	8.89	9.91	10.87	8.65	10.25	13.09
EAU / INPUT	4.60	7.59	8.18	6.84	6.86	7.66	6.99
CO / INPUT	49.65	44.60	40.51	34.33	28.43	31.19	27.67
CO2 / INPUT	23.53	28.01	34.46	38.59	33.46	40.60	49.73
H2 / INPUT	2.98	2.86	2.86	2.85	2.17	2.45	2.23
BILAN MASSE (%wt)	89.97	93.66	96.47	96.88	82.14	95.59	103.95
SELECTIVITE: (% wt)							
C1/HC TOTAUX	31.23	29.66	28.09	26.62	27.04	26.13	26.12
C2/HC TOTAUX	14.84	13.96	13.24	12.68	13.16	12.78	12.63
C3/HC TOTAUX	16.39	17.28	17.04	16.26	17.29	16.97	16.61
C4/HC TOTAUX	22.70	19.49	17.80	15.46	16.24	15.70	14.73
C5+/HC TOTAUX	14.85	19.61	23.84	28.98	26.28	28.42	28.91
P O N A (%wt)							
P / HC (LIQ)	45.45	54.41	56.76	55.41	59.62	54.70	55.73
O / HC (LIQ)	28.04	26.52	25.55	29.88	21.54	29.51	27.00
N / HC (LIQ)	11.38	8.33	7.94	6.81	9.22	7.38	8.73
A / HC (LIQ)	15.13	10.75	9.75	7.90	9.62	8.41	8.55

TABLE A3

RAPPORT GAZ DE SYNTHESE								
DATE	06-Dec-86	08-Dec-86	10-Dec-86	12-Dec-86	14-Dec-86	16-Dec-86	18-Dec-86	
CATALYSEUR	ZKQ-4A-Na	ZKQ-4A-Na	ZKQ-4A-Na	ZKQ-4A-Na	ZKQ-4A-Na	ZKQ-4A-Na	ZKQ-4A-Na	
ESSAI #	2	2	2	2	2	2	2	
# HEURES D'ESSAI	48	48	48	48	48	48	48	
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336	
POIDS CATALYSEUR (g)	6.24	6.24	6.24	6.24	6.24	6.24	6.24	
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	
GHSV (ml/h)/ml	300	300	300	300	300	300	300	
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020	
T1 (°C)	300	300	300	300	300	300	300	
RATIO (H2/CO)	1.00	0.99	0.98	1.00	0.98	1.00	0.97	
CONVERSION H2 (%wt)	59.33	60.32	61.78	61.62	63.67	65.13	65.41	
CONVERSION CO (%wt)	70.31	69.94	70.91	71.73	73.52	74.96	76.90	
CONVERSION TOTALE (%wt)	69.57	69.30	70.31	71.05	72.87	74.29	76.15	
PRODUITS (%wt)								
HC TOTAL / INPUT	12.38	13.17	13.82	14.52	14.39	14.95	15.25	
HC (LIQ) / INPUT	2.46	3.25	3.35	3.68	3.67	3.95	4.43	
HC (GAZ) / INPUT	9.92	9.92	10.47	10.84	10.72	11.00	10.82	
EAU / INPUT	3.92	6.62	6.69	7.94	6.28	7.40	7.72	
CO / INPUT	27.70	28.05	27.17	26.37	24.72	23.36	21.59	
CO2 / INPUT	40.91	37.99	39.42	42.09	42.36	43.66	43.61	
H2 / INPUT	2.73	2.65	2.52	2.57	2.41	2.35	2.26	
BILAN MASSE (%wt)	87.63	88.48	89.61	93.49	90.16	91.71	90.42	
SELECTIVITE: (C1-C4)/C5+	4.04	3.05	3.12	2.95	2.92	2.79	2.44	
P O N A (%wt)								
P / HC (LIQ)	26.04	30.43	27.18	27.84	28.36	30.48	29.58	
O / HC (LIQ)	54.08	47.78	54.23	54.09	54.95	52.25	52.75	
N / HC (LIQ)	9.28	10.13	8.83	8.63	8.09	8.61	8.10	
A / HC (LIQ)	9.88	11.67	9.76	9.43	8.59	8.66	9.57	
C1/HC TOTAUX	25.75	23.08	23.13	23.47	23.26	22.63	21.86	
C2/HC TOTAUX	15.03	13.07	13.11	13.06	12.87	12.40	11.84	
C3/HC TOTAUX	14.18	15.03	15.89	16.67	17.05	17.00	16.70	
C4/HC TOTAUX	22.09	21.00	20.80	19.58	19.18	19.14	17.77	
C5+/HC TOTAUX	22.94	27.81	27.08	27.21	27.64	28.82	31.83	

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)								DIESEL
IBP	76	66	88	84	57	73	85	124
10	111	99	117	117	98	111	116	201
20	124	116	128	129	115	125	127	226
30	131	126	142	141	126	140	142	246
50	151	149	163	167	152	164	166	281
70	171	174	188	196	184	196	196	317
80	186	191	205	216	206	220	216	336
90	205	214	232	255	243	263	254	360
FBP	278	277	356	383	369	370	361	415

TABLE A4

RAPPORT GAZ DE SYNTHESE

DATE	06-Dec-86	08-Dec-86	10-Dec-86	12-Dec-86	14-Dec-86	16-Dec-86	18-Dec-86	
CATALYSEUR	ZKQ-4A-Co	ZKQ-4A-Co	ZKQ-4A-Co	ZKQ-4A-Co	ZKQ-4A-Co	ZKQ-4A-Co	ZKQ-4A-Co	(Na +5%La)
ESSAI #	3	3	3	3	3	3	3	
# HEURES D'ESSAI	48	48	48	48	48	48	48	
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336	
POIDS CATALYSEUR (g)	6.98	6.98	6.98	6.98	6.98	6.98	6.98	
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	
GHSV (ml/h)/ml	300	300	300	300	300	300	300	
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020	
T1 (°C)	300	300	300	300	300	300	300	
RATIO (H2/CO)	1.03	1.02	1.00	1.03	1.04	1.06	1.02	
CONVERSION H2 (%wt)	61.68	63.03	64.44	63.37	63.23	63.46	64.19	
CONVERSION CO (%wt)	80.82	83.03	83.40	83.69	83.97	84.00	84.35	
CONVERSION TOTALE (%wt)	79.50	81.67	82.13	82.30	82.52	82.54	82.96	
PRODUITS (%wt)								
HC TOTAL / INPUT	15.25	17.83	17.39	18.18	17.84	18.33	18.28	
HC (LIQ) / INPUT	3.09	5.18	4.69	4.77	4.63	5.21	5.26	
HC (GAZ) / INPUT	12.16	12.65	12.70	13.41	13.21	13.12	13.02	
EAU / INPUT	1.64	5.19	5.43	6.12	5.11	5.95	6.06	
CO / INPUT	17.86	15.81	15.48	15.17	14.91	14.87	14.58	
CO2 / INPUT	53.91	54.60	56.98	57.65	56.86	57.29	57.77	
H2 / INPUT	2.64	2.53	2.38	2.53	2.57	2.59	2.46	
BILAN MASSE (%wt)	91.31	95.96	97.67	99.66	97.29	99.04	99.14	
SELECTIVITE: (C1-C4)/C5+	3.93	2.44	2.71	2.81	2.85	2.52	2.48	
P O N A (%wt)								
P / HC (LIQ)	31.79	32.47	30.56	31.29	33.33	35.05	36.60	
O / HC (LIQ)	44.21	48.25	53.33	53.20	51.13	49.02	48.52	
N / HC (LIQ)	12.32	9.94	8.57	8.45	7.93	9.10	8.52	
A / HC (LIQ)	11.68	9.34	7.54	6.96	7.61	6.83	6.37	
C1/HC TOTAUX	29.36	26.23	26.61	25.91	25.68	24.52	23.51	
C2/HC TOTAUX	14.92	12.68	13.11	12.83	12.79	12.34	12.00	
C3/HC TOTAUX	12.06	10.72	11.72	12.63	13.62	14.00	14.28	
C4/HC TOTAUX	18.63	17.01	17.82	18.08	18.24	17.58	17.91	
C5+/HC TOTAUX	25.03	33.36	30.74	30.55	29.67	31.58	32.31	

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)								DIESEL
IBP	85	40	42	93	39	71	67	124
10	114	86	87	121	88	108	100	201
20	125	101	101	131	102	125	118	226
30	132	118	118	144	120	139	128	246
50	151	141	142	164	145	164	156	281
70	170	166	168	188	174	196	192	317
80	184	183	187	202	195	219	215	336
90	204	207	212	226	227	266	253	360
FBP	305	301	306	306	356	415	391	415

TABLE A5

RAPPORT GAZ DE SYNTHESE

DATE	22-Jan-87	24-Jan-87	26-Jan-87	28-Jan-87	30-Jan-87	01-Feb-87	03-Feb-87
CATALYSEUR	ZKQIB4A-.3	ZKQIB4A-.3	ZKQIB4A-.3	ZKQIB4A-.3	ZKQIB4A-.3	ZKQIB4A-.3	ZKQIB4A-.3Na
ESSAI #	4	4	4	4	4	4	4
# HEURES D'ESSAI	48	48	48	48	48	48	48
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336
POIDS CATALYSEUR (g)	5.78	5.78	5.78	5.78	5.78	5.78	5.78
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020
TI (°C)	300	300	300	300	300	300	300
RATIO (H2/CO)	1.06	1.12	1.05	1.03	1.04	1.07	1.08
CONVERSION H2 (%wt)	60.88	61.30	63.03	64.45	64.76	65.30	65.79
CONVERSION CO (%wt)	66.40	65.85	69.84	72.96	74.22	75.73	77.48
CONVERSION TOTALE (%wt)	66.01	65.51	69.36	72.37	73.56	74.99	76.64
PRODUITS (%wt)							
HC TOTAL / INPUT	12.55	14.46	14.14	14.85	15.25	15.96	16.71
HC (LIQ) / INPUT	2.34	3.72	4.15	4.72	4.86	4.96	5.38
HC (GAZ) / INPUT	10.21	10.74	9.99	10.13	10.39	10.99	11.32
EAU / INPUT	4.05	8.26	7.30	6.82	7.15	6.96	7.70
CO / INPUT	31.21	31.59	28.05	25.17	23.97	22.53	20.89
CO2 / INPUT	39.41	39.75	39.72	41.45	43.13	45.64	47.77
H2 / INPUT	2.78	2.90	2.59	2.46	2.47	2.48	2.47
BILAN MASSE (%wt)	90.00	96.95	91.80	90.74	91.97	93.58	95.54
SELECTIVITE:(C1-C4)/C5+	4.37	2.89	2.41	2.15	2.14	2.22	2.10
P O N A (%wt)							
P / HC (LIQ)	32.46	37.87	40.93	41.01	42.03	44.51	45.38
O / HC (LIQ)	48.62	45.07	44.58	44.00	43.31	40.09	40.05
N / HC (LIQ)	10.50	9.02	8.27	8.22	8.04	8.48	7.97
A / HC (LIQ)	8.43	8.04	6.21	6.77	6.61	6.91	6.60
C1/HC TOTAUX	25.33	22.60	21.27	20.38	20.49	20.71	20.83
C2/HC TOTAUX	15.50	12.97	11.83	11.17	10.94	10.85	10.72
C3/HC TOTAUX	16.51	17.85	17.34	16.72	16.54	16.54	16.03
C4/HC TOTAUX	20.93	18.17	17.36	16.98	16.23	16.55	16.27
C5+/HC TOTAUX	21.72	28.41	32.19	34.75	35.80	35.34	36.15

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)								DIESEL
IBP	34	75	71	32	34	35	29	130
10	96	115	114	88	88	95	93	206
20	114	128	128	110	109	115	114	231
30	124	145	147	125	125	129	127	251
50	147	171	174	156	156	164	164	286
70	169	206	213	195	195	206	206	318
80	184	232	245	227	227	236	238	335
90	205	269	284	270	270	285	286	357
FBP	277	382	379	358	363	422	414	412

TABLE A6

RAPPORT GAZ DE SYNTHESE							
DATE	22-Jan-87	24-Jan-87	26-Jan-87	28-Jan-87	30-Jan-87	01-Feb-87	03-Feb-87
CATALYSEUR	ZKQIB4A-.5	ZKQIB4A-.5	ZKQIB4A-.5	ZKQIB4A-.5	ZKQIB4A-.5	ZKQIB4A-.5	ZKQIB4A-.5Na
ESSAI #	5	5	5	5	5	5	5
# HEURES D'ESSAI	48	48	48	48	48	48	48
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336
POIDS CATALYSEUR (g)	5.61	5.61	5.61	5.61	5.61	5.61	5.61
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020
TI ('C)	300	300	300	300	300	300	300
RATIO (H2/CO)	1.09	1.12	1.05	1.05	1.11	1.14	1.15
CONVERSION H2 (%wt)	58.32	56.68	58.99	59.89	61.99	62.06	61.76
CONVERSION CO (%wt)	67.60	64.91	70.42	71.53	72.17	72.31	72.73
CONVERSION TOTALE (%wt)	66.93	64.30	69.61	70.72	71.42	71.53	71.89
PRODUITS (%wt)							
HC TOTAL / INPUT	12.84	15.27	14.71	15.32	15.58	16.02	16.80
HC (LIQ) / INPUT	2.14	2.77	2.84	3.17	3.23	3.33	4.00
HC (GAZ) / INPUT	10.70	12.50	11.86	12.15	12.35	12.69	12.80
EAU / INPUT	3.34	6.50	6.82	6.77	6.34	6.96	6.75
CO / INPUT	30.04	32.47	27.49	26.47	25.77	25.59	25.18
CO2 / INPUT	43.05	46.22	44.11	45.94	47.59	49.44	50.33
H2 / INPUT	3.04	3.23	2.89	2.81	2.81	2.88	2.93
BILAN MASSE (%wt)	92.30	103.69	96.02	97.32	98.09	100.88	102.18
SELECTIVITE: (C1-C4)/C5+	5.01	4.51	4.17	3.83	3.83	3.81	3.20
P O N A (%wt)							
P / HC (LIQ)	25.26	28.17	29.40	29.33	30.46	31.39	32.58
O / HC (LIQ)	55.34	51.45	53.11	52.64	50.93	47.44	47.25
N / HC (LIQ)	10.24	9.30	8.94	9.07	10.11	9.53	8.98
A / HC (LIQ)	9.16	11.08	8.55	8.96	8.49	11.64	11.19
C1/HC TOTAUX	27.04	24.90	24.82	24.24	24.35	24.40	23.57
C2/HC TOTAUX	15.60	14.20	13.95	13.60	13.63	13.59	13.00
C3/HC TOTAUX	15.10	19.15	19.79	19.93	20.32	20.42	19.72
C4/HC TOTAUX	22.61	20.83	19.76	19.01	18.88	18.52	17.62
C5+/HC TOTAUX	19.65	20.93	21.67	23.22	22.82	23.07	26.09
DISTILLATION SIMULEE ASTM D2887							
% OFF (C)							DIESEL
IBP	67	71	74	73	33	36	33	130
10	98	109	112	112	86	96	95	206
20	115	123	125	124	101	114	114	231
30	124	135	138	138	122	126	126	251
50	144	154	160	160	148	159	159	286
70	165	179	186	186	179	193	194	318
80	178	195	204	204	201	218	221	335
90	198	218	231	232	234	268	272	357
FBP	275	282	315	327	336	411	416	412

TABLE A7

RAPPORT GAZ DE SYNTHESE

DATE	08-Mar-87	10-Mar-87	12-Mar-87	14-Mar-87	16-Mar-87	18-Mar-87	20-Mar-87	
CATALYSEUR	Co,.3Na-ZKCo,	.3Na-ZKCo,	.3Na-ZKCo,	.3Na-ZKCo,	.3Na-ZKCo,	.3Na-ZKCo,	.3Na-ZKDIB-4A(La)	
ESSAI #	6	6	6	6	6	6	6	
# HEURES D'ESSAI	48	48	48	48	48	48	48	
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336	
POIDS CATALYSEUR (g)	6.50	6.50	6.50	6.50	6.50	6.50	6.50	
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	
GHSV (ml/h)/ml	305	305	305	305	305	305	305	
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020	
T1 ('C)	300	300	300	300	300	300	300	
RATIO (H2/CO)	1.06	1.06	1.00	1.03	1.04	1.06	1.07	
CONVERSION H2 (%wt)	57.24	58.68	59.47	57.95	58.43	58.28	59.13	
CONVERSION CO (%wt)	62.88	63.59	64.86	63.95	64.39	63.59	64.47	
CONVERSION TOTALE (%wt)	62.48	63.24	64.50	63.54	63.97	63.21	64.09	
PRODUITS (%wt)								
HC TOTAL / INPUT	11.37	13.12	12.97	13.68	13.64	13.62	14.05	
HC (LIQ) / INPUT	1.17	2.83	3.20	3.41	3.75	4.01	4.42	
HC (GAZ) / INPUT	10.20	10.29	9.77	10.27	9.89	9.61	9.62	
EAU / INPUT	3.43	6.99	6.54	7.07	7.21	6.75	9.57	
CO / INPUT	34.48	33.82	32.77	33.55	33.12	33.84	32.99	
CO2 / INPUT	38.07	38.99	36.33	37.21	36.07	35.54	35.65	
H2 / INPUT	3.04	2.95	2.74	2.91	2.91	2.95	2.92	
BILAN MASSE (%wt)	90.39	95.87	91.35	94.42	92.95	92.70	95.18	
SELECTIVITE: (C1-C4)/C5+	8.75	3.64	3.06	3.01	2.63	2.40	2.18	
P O N A (%wt)								
P / HC (LIQ)	34.05	34.76	33.77	33.34	35.19	32.65	35.37	
O / HC (LIQ)	47.64	48.23	50.24	48.92	46.30	47.39	42.95	
N / HC (LIQ)	9.48	8.89	7.98	9.74	10.02	12.06	10.17	
A / HC (LIQ)	8.83	8.12	8.01	7.99	8.50	7.91	11.50	
C1/HC TOTAUX	28.95	24.13	24.52	24.16	23.53	23.68	23.31	
C2/HC TOTAUX	13.64	11.97	11.51	11.30	10.99	10.94	10.59	
C3/HC TOTAUX	19.61	19.15	18.64	18.17	17.44	17.22	16.62	
C4/HC TOTAUX	23.56	19.67	17.77	17.23	16.28	15.74	14.97	
C5+/HC TOTAUX	14.24	25.08	27.57	29.14	31.75	32.43	34.50	

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)								DIESEL
IBP	38	30	27	32	32	19	26	126
10	93	85	86	89	94	87	93	201
20	111	101	106	108	112	100	113	226
30	123	122	122	122	124	123	125	246
50	145	148	148	150	154	149	162	281
70	166	178	184	187	190	187	203	315
80	180	199	209	212	214	212	233	333
90	200	231	249	258	259	252	289	356
FBP	294	350	364	362	361	356	436	411

TABLE A8

RAPPORT GAZ DE SYNTHESE

DATE	08-Mar-87	10-Mar-87	12-Mar-87	14-Mar-87	16-Mar-87	18-Mar-87	20-Mar-87
CATALYSEUR	Co,.5Na-ZKCo,	.5Na-ZKCo,	.5Na-ZKCo,	.5Na-ZKCo,	.5Na-ZKCo,	.5Na-ZKCo,	.5Na-ZKCo/B-4A(La)
ESSAI #	7	7	7	7	7	7	7
# HEURES D'ESSAI	48	48	48	48	48	48	48
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336
POIDS CATALYSEUR (g)	6.34	6.34	6.34	6.34	6.34	6.34	6.34
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	385	385	341	341	341	341	341
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020
T1 (°C)	300	300	300	300	300	300	300
RATIO (H2/CO)	1.24	1.26	0.97	0.99	1.02	1.04	1.05
CONVERSION H2 (%wt)	52.18	52.57	56.88	56.69	56.13	56.65	56.49
CONVERSION CO (%wt)	61.15	60.92	61.16	61.79	61.39	61.28	60.98
CONVERSION TOTALE (%wt)	60.41	60.23	60.88	61.45	61.22	60.95	60.67
PRODUITS (%wt)							
HC TOTAL / INPUT	13.05	13.90	13.00	13.32	13.19	13.66	14.18
HC (LIQ) / INPUT	0.60	2.07	3.33	4.08	4.33	5.09	5.58
HC (GAZ) / INPUT	12.46	11.83	9.66	9.24	8.86	8.57	8.60
EAU / INPUT	4.23	8.33	6.00	6.22	6.24	5.22	6.39
CO / INPUT	35.65	35.83	36.30	35.66	35.77	36.03	36.28
CO2 / INPUT	36.05	35.48	36.82	36.67	36.33	35.97	36.66
H2 / INPUT	3.93	3.94	2.83	2.89	3.01	3.01	3.05
BILAN MASSE (%wt)	92.92	97.48	94.94	94.75	94.54	93.90	96.56
SELECTIVITE:(C1-C4)/C5+	20.85	5.72	2.90	2.27	2.05	1.68	1.54
P O N A (%wt)							
P / HC (LIQ)	42.07	45.08	43.30	44.36	44.74	43.36	43.55
O / HC (LIQ)	35.41	34.54	37.34	36.69	35.96	38.46	38.97
N / HC (LIQ)	11.80	11.40	10.41	9.80	9.58	8.70	8.92
A / HC (LIQ)	10.72	8.98	8.95	9.16	9.72	9.49	8.56
C1/HC TOTAUX	32.04	28.45	24.60	22.79	22.11	20.53	19.55
C2/HC TOTAUX	15.50	14.13	12.03	10.89	10.38	9.53	9.08
C3/HC TOTAUX	21.96	20.27	18.71	17.20	16.66	15.70	15.30
C4/HC TOTAUX	19.27	16.76	15.73	14.75	14.46	13.79	13.45
C5+/HC TOTAUX	11.23	20.38	28.93	34.37	36.38	40.44	42.62

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)								DIESEL
IBP	42	36	36	39	37	34	36	126
10	99	97	98	99	99	97	98	201
20	123	122	123	125	124	123	124	226
30	137	138	143	147	147	146	147	246
50	157	163	172	183	184	186	187	281
70	177	191	213	230	230	234	238	315
80	192	209	247	268	267	273	276	333
90	212	235	291	321	325	329	335	356
FBP	310	314	398	421	432	444	453	411

TABLE A9

RAPPORT GAZ DE SYNTHESE									
DATE		12-May-87	14-May-87	16-May-87	18-May-87	20-May-87	22-May-87	24-May-87	26-May-87
CATALYSEUR		ZKQ4A.3Na+ZKQ4A.3Na+ZKQ4A.3Na+ZKQ4A.3Na+ZKQ4A.3Na+ZKQ4A.3Na+ZKQ4A.3Na+ZKQ4A.3Na+Acide Stearique							
ESSAI #		8	8	8	8	8	8	8	8
# HEURES D'ESSAI		48	48	48	48	48	48	48	48
TEMPS D'ESSAI TOTAL		48	96	144	192	240	288	336	384
POIDS CATALYSEUR (g)		4.65	4.65	4.65	4.65	4.65	4.65	4.65	4.65
VOL. CATALYSEUR (ml)		8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml		300	300	300	300	300	300	300	300
PRESSION kPa		1020	1020	1020	1020	1020	1020	1020	1020
T1 ('C)		300	300	300	300	300	300	300	300
RATIO (H2/CO)		1.00	0.95	1.02	1.01	0.96	0.97	0.96	0.96
CONVERSION H2 (%wt)		58.91	60.39	62.26	62.98	64.75	64.33	64.99	65.28
CONVERSION CO (%wt)		62.01	65.07	67.77	68.93	72.18	71.85	73.50	73.99
CONVERSION TOTALE (%wt)		61.80	64.77	67.40	68.52	71.69	71.35	72.95	73.43
PRODUITS (%wt)									
HC TOTAL / INPUT		10.83	12.02	13.11	14.14	13.84	14.49	15.02	14.77
HC (LIQ) / INPUT		1.11	2.03	2.06	2.40	2.37	2.54	2.72	2.65
HC (GAZ) / INPUT		9.72	10.00	11.06	11.74	11.47	11.95	12.30	12.12
EAU / INPUT		3.46	5.35	5.83	7.12	5.87	5.32	6.34	6.75
CO / INPUT		35.43	32.69	30.02	28.96	26.02	26.31	24.78	24.32
CO2 / INPUT		34.52	34.17	37.64	40.55	40.03	41.31	42.28	42.65
H2 / INPUT		2.77	2.54	2.58	2.52	2.29	2.33	2.27	2.25
BILAN MASSE (%wt)		87.04	86.77	89.19	93.29	88.04	89.76	90.68	90.74
SELECTIVITE:(C1-C4)/C5+		8.72	4.93	5.37	4.88	4.85	4.71	4.53	4.57
P O N A (%wt)									
P / HC (LIQ)		28.74	28.91	28.63	29.40	29.15	29.39	29.47	30.82
O / HC (LIQ)		45.54	47.31	46.82	47.52	48.13	47.37	48.69	47.75
N / HC (LIQ)		13.00	11.34	12.03	11.08	10.64	11.49	10.91	10.89
A / HC (LIQ)		12.72	12.45	12.53	12.01	12.08	11.75	10.93	10.54
C1/HC TOTAUX		26.61	23.51	24.55	24.49	23.32	22.36	23.32	23.85
C2/HC TOTAUX		15.76	15.03	14.22	14.06	13.75	13.59	13.17	13.33
C3/HC TOTAUX		19.21	19.05	20.39	20.57	20.50	20.93	20.26	20.19
C4/HC TOTAUX		24.45	21.72	21.46	20.34	20.24	20.84	19.44	19.28
C5+/HC TOTAUX		13.98	20.70	19.38	20.54	22.18	22.27	23.81	23.35
DISTILLATION SIMULEE ASTM D2887									
% OFF (C)									DIESEL
	IBP	37	33	33	32	31	30	27	26	116
	10	93	91	89	90	90	88	90	86	192
	20	110	110	108	109	109	108	109	107	216
	30	122	122	120	122	122	122	123	120	234
	50	145	148	146	149	150	149	155	148	271
	70	165	176	174	179	181	181	188	180	307
	80	180	193	191	199	202	202	213	202	326
	90	200	219	217	229	237	237	259	237	351
	FBP	295	342	313	352	369	363	370	355	405

TABLE A10

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RAPPORT GAZ DE SYNTHESE

****

DATE	18-May-87	20-May-87	22-May-87	24-May-87	26-May-87
CATALYSEUR	ZKQ4A.3Na	ZKQ4A.3Na	ZKQ4A.3Na	ZKQ4A.3Na	ZKQ4A.3Na
ESSAI #	9A	9A	9A	9A	9A
# HEURES D'ESSAI	48	48	48	48	48
TEMPS D'ESSAI TOTAL	48	96	144	192	240
POIDS CATALYSEUR (g)	5.54	5.54	5.54	5.54	5.54
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020
T1 (°C)	300	300	300	300	300
RATIO (H2/CO)	0.96	0.93	0.92	0.92	0.93
CONVERSION H2 (%wt)	63.19	65.49	66.51	67.26	67.81
CONVERSION CO (%wt)	67.66	73.31	75.94	77.72	78.40
CONVERSION TOTALE (%wt)	67.37	72.82	75.35	77.06	77.74
PRODUITS (%wt)					
HC TOTAL / INPUT	10.92	12.86	13.79	14.29	14.86
HC (LIQ) / INPUT	1.22	2.72	3.23	3.52	4.22
HC (GAZ) / INPUT	9.71	10.14	10.56	10.77	10.65
EAU / INPUT	2.12	5.71	5.27	5.03	5.72
CO / INPUT	30.24	25.01	22.56	20.89	20.24
CO2 / INPUT	37.70	40.66	43.86	45.13	45.55
H2 / INPUT	2.38	2.17	2.09	2.05	2.02
BILAN MASSE (%wt)	83.37	86.41	87.57	87.39	88.40
SELECTIVITE:(C1-C4)/C5+	7.98	3.72	3.27	3.06	2.57
P O N A (%wt)					
P / HC (LIQ)	27.98	29.68	30.86	31.83	31.95
O / HC (LIQ)	47.07	48.77	47.39	46.76	48.02
N / HC (LIQ)	13.03	11.95	11.09	11.04	10.57
A / HC (LIQ)	11.92	9.60	10.66	10.37	9.47
C1/HC TOTAUX	26.38	22.73	22.12	21.58	20.41
C2/HC TOTAUX	15.75	13.63	13.05	12.58	11.76
C3/HC TOTAUX	19.39	18.99	19.17	18.93	18.13
C4/HC TOTAUX	23.52	20.32	19.34	18.80	17.69
C5+/HC TOTAUX	14.96	24.33	26.32	28.11	32.00

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)						DIESEL
IBP	36	32	32	31	32	116
10	92	90	91	93	92	192
20	109	110	110	112	112	216
30	120	122	123	130	129	234
50	142	149	154	159	159	271
70	164	181	187	198	199	307
80	179	202	210	227	228	326
90	203	204	253	278	279	351
FBP	307	354	397	422	419	405

14 MAI RECONDITIONNE LE REACTEUR # 2

TABLE A11

RAPPORT GAZ DE SYNTHESE

DATE	05-Jun-87	07-Jun-87	09-Jun-87	11-Jun-87	13-Jun-87	15-Jun-87	17-Jun-87	19-Jun-87
CATALYSEUR	ZKQIB4A-R1	ZKQIB4A-R1	ZKQIB4A-R1	ZKQIB4A-R1	ZKQIB4A-R1	ZKQIB4A-R1	ZKQIB4A-R1	ZKQIB4A-R1
ESSAI #	10	10	10	10	10	10	10	10
# HEURES D'ESSAI	48	48	48	48	48	48	48	48
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336	384
POIDS CATALYSEUR (g)	6.41	6.41	6.41	6.41	6.41	6.41	6.41	6.41
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1020	2721	2721
T1 (°C)	275	275	300	300	300	300	300	300
RATIO (H2/CO)	0.98	0.97	0.99	0.98	1.00	0.98	1.00	0.97
CONVERSION H2 (%wt)	53.35	50.04	58.88	58.35	58.72	58.63	78.92	76.87
CONVERSION CO (%wt)	47.13	41.01	58.31	57.86	57.42	58.36	76.46	69.47
CONVERSION TOTALE (%wt)	47.54	41.60	58.35	57.90	57.51	58.38	76.63	69.95
PRODUITS (%wt)								
HC TOTAL / INPUT	8.45	8.91	13.63	12.02	12.20	12.54	17.49	16.05
HC (LIQ) / INPUT	0.47	1.84	2.44	1.73	1.63	1.75	4.04	3.60
HC (GAZ) / INPUT	7.98	7.07	11.19	10.29	10.57	10.80	13.45	12.45
EAU / INPUT	5.06	8.07	6.19	7.41	7.73	6.77	11.19	11.78
CO / INPUT	49.37	55.12	38.90	39.36	39.71	38.89	21.95	28.53
CO2 / INPUT	21.06	16.61	32.49	30.63	30.99	30.90	38.95	32.75
H2 / INPUT	3.09	3.28	2.75	2.75	2.78	2.74	1.42	1.51
BILAN MASSE (%wt)	87.03	91.99	93.96	92.17	93.41	91.84	91.00	90.60
SELECTIVITE:(C1-C4)/C5+	17.04	3.85	4.59	5.95	6.48	6.19	3.33	3.46
P O N A (%wt)								
P / HC (LIQ)	0.00	42.71	37.93	36.67	35.41	35.57	39.22	39.90
O / HC (LIQ)	0.00	32.24	39.29	38.46	40.50	41.12	40.89	39.23
N / HC (LIQ)	0.00	12.82	11.18	12.53	12.69	12.40	10.01	10.30
A / HC (LIQ)	0.00	12.23	11.60	12.34	11.41	10.91	9.88	10.57
C1/HC TOTAUX	25.41	21.25	25.07	27.25	27.73	27.11	23.28	24.34
C2/HC TOTAUX	14.70	12.34	12.76	13.42	13.38	12.91	12.71	12.32
C3/HC TOTAUX	21.65	20.94	18.50	18.44	18.78	18.40	17.42	19.12
C4/HC TOTAUX	24.90	19.25	19.53	21.28	21.37	20.98	16.68	16.48
C5+/HC TOTAUX	13.34	26.22	24.14	19.61	18.74	20.60	29.91	27.74

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)									DIESEL
IBP	0	42	36	39	39	34	19	31	117
10	0	116	96	96	95	94	91	95	192
20	0	136	121	119	119	117	117	121	216
30	0	148	139	136	135	132	134	143	234
50	0	178	167	160	160	157	162	178	271
70	0	209	200	189	187	183	197	221	307
80	0	231	221	209	207	202	221	255	325
90	0	270	258	246	243	229	264	307	350
FBP	0	370	361	367	374	344	392	446	405

TABLE A12

RAPPORT GAZ DE SYNTHESE

DATE	05-Jun-87	07-Jun-87	09-Jun-87	11-Jun-87	13-Jun-87	15-Jun-87	17-Jun-87	19-Jun-87
CATALYSEUR	ZKQIB4A-R2	ZKQIB4A-R2	ZKQIB4A-R2	ZKQIB4A-R2	ZKQIB4A-R2	ZKQIB4A-R2	ZKQIB4A-R2	ZKQIB4A-R2
ESSAI #	11	11	11	11	11	11	11	11
# HEURES D'ESSAI	48	48	48	48	48	48	48	48
TEMPS D'ESSAI TOTAL	48	96	144	192	240	288	336	384
POIDS CATALYSEUR (g)	6.28	6.28	6.28	6.28	6.28	6.28	6.28	6.28
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1020	2721	2721
T1 (°C)	275	275	300	300	300	300	300	300
RATIO (H2/CO)	0.91	0.91	0.93	0.92	0.92	0.92	0.93	0.90
CONVERSION H2 (%wt)	57.37	55.06	71.88	71.60	71.21	71.16	79.70	79.62
CONVERSION CO (%wt)	52.99	50.74	81.39	79.94	78.97	79.33	85.09	83.33
CONVERSION TOTALE (%wt)	53.26	51.00	80.79	79.42	78.49	78.83	84.75	83.11
PRODUITS (%wt)								
HC TOTAL / INPUT	9.33	10.80	18.03	16.73	16.84	17.24	17.94	18.74
HC (LIQ) / INPUT	0.38	1.69	2.30	2.21	2.59	3.25	4.24	4.76
HC (GAZ) / INPUT	8.95	9.11	15.73	14.53	14.25	13.98	13.70	13.98
EAU / INPUT	2.71	6.80	4.63	4.16	4.30	4.48	6.06	6.97
CO / INPUT	44.12	46.22	17.45	18.82	19.72	19.38	13.98	15.66
CO2 / INPUT	26.69	27.92	54.91	52.33	51.77	51.72	51.21	50.18
H2 / INPUT	2.62	2.76	1.76	1.76	1.79	1.79	1.27	1.24
BILAN MASSE (%wt)	85.47	94.51	96.77	88.87	94.42	94.61	90.46	92.78
SELECTIVITE:(C1-C4)/C5+	23.52	5.39	6.84	6.59	5.50	4.30	3.23	2.94
P O N A (%wt)								
P / HC (LIQ)	0.00	44.55	44.03	40.83	40.68	40.86	43.80	47.11
O / HC (LIQ)	0.00	33.86	36.50	39.44	40.33	40.41	39.28	36.38
N / HC (LIQ)	0.00	9.46	9.50	10.52	9.72	9.19	7.84	6.76
A / HC (LIQ)	0.00	12.12	9.97	9.21	9.26	9.54	9.08	9.75
C1/HC TOTAUX	25.85	22.10	27.24	26.81	25.74	24.92	21.52	20.96
C2/HC TOTAUX	15.48	13.24	14.21	13.70	12.99	12.44	12.64	12.16
C3/HC TOTAUX	24.99	22.83	21.82	21.88	21.42	20.66	20.00	19.90
C4/HC TOTAUX	22.31	20.68	17.88	18.72	18.42	17.48	16.64	16.51
C5+/HC TOTAUX	11.37	21.14	18.85	18.89	21.43	24.50	29.20	30.48

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)									DIESEL
IBP	0	36	32	35	33	31	30	30	117
10	0	99	95	95	94	94	94	94	192
20	0	123	121	119	118	119	120	120	216
30	0	144	139	137	134	137	141	142	234
50	0	168	169	166	161	150	176	174	271
70	0	197	208	203	198	205	221	219	307
80	0	213	236	230	226	235	258	254	325
90	0	239	279	279	270	281	311	307	350
FBP	0	323	375	389	387	399	429	409	405

TABLE A13

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RAPPORT GAZ DE SYNTHESE

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DATE	27-Sep-87	29-Sep-87	02-Oct-87
CATALYSEUR	Co.Na-ZKQIB4A(La)	Co.Na-ZKQIB4A(La)	Co.Na-ZKQIB4A(La)
ESSAI #	12	12	12
# HEURES D'ESSAI	47	48	72
TEMPS D'ESSAI TOTAL	47	95	167
POIDS CATALYSEUR (g)	5.80	5.80	5.80
VOL. CATALYSEUR (ml)	8.00	8.00	8.00
GHSV (ml/h)/ml	299	299	299
PRESSION kPa	1020	1020	1020
T1 (°C)	300	300	300
RATIO (H2/CO)	1.00	0.97	1.03
CONVERSION H2 (%wt)	46.73	47.14	47.80
CONVERSION CO (%wt)	44.60	44.76	44.83
CONVERSION TOTALE (%wt)	44.74	44.92	45.04
PRODUITS (%wt)			
HC TOTAL / INPUT	7.82	9.13	10.08
HC (LIQ) / INPUT	0.64	2.58	3.10
HC (GAZ) / INPUT	7.18	6.55	6.98
EAU / INPUT	2.15	7.01	7.04
CO / INPUT	51.66	51.62	51.36
CO2 / INPUT	26.08	23.88	25.62
H2 / INPUT	3.60	3.47	3.60
BILAN MASSE (%wt)	91.31	95.11	97.70
SELECTIVITE:(C1-C4)/C5+	11.19	2.54	2.25
P O N A (%wt)			
P / HC (LIQ)	41.63	44.46	45.71
O / HC (LIQ)	29.59	29.69	30.68
N / HC (LIQ)	13.15	9.98	8.54
A / HC (LIQ)	15.63	15.94	15.07
C1/HC TOTAUX	27.21	21.48	20.97
C2/HC TOTAUX	15.91	12.31	11.65
C3/HC TOTAUX	24.61	19.43	18.51
C4/HC TOTAUX	21.14	16.41	15.75
C5+/HC TOTAUX	11.13	30.37	33.11

DISTILLATION SIMULEE
ASTM D2887

% OFF (C)				Diesel
IBP	49	51	43	124
10	111	119	119	198
20	123	143	142	222
30	143	159	157	242
50	162	189	188	278
70	184	228	227	311
80	199	258	258	329
90	218	297	302	351
FBP	292	403	386	405

CRIQ

TABLE A14

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RAPPORT GAZ DE SYNTHESE

****

DATE	27-Sep-87	29-Sep-87	02-Oct-87
CATALYSEUR	Zn-ZKQIB4A(La)	Zn-ZKQIB4A(La)	Zn-ZKQIB4A(La)
ESSAI #	13	13	13
# HEURES D'ESSAI	47	48	72
TEMPS D'ESSAI TOTAL	47	95	167
POIDS CATALYSEUR (g)	6.29	6.29	6.29
VOL. CATALYSEUR (ml)	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300
PRESSION kPa	1020	1020	1020
T1 (°C)	300	300	300
RATIO (H2/CO)	1.04	1.01	1.03
CONVERSION H2 (%wt)	56.35	63.49	65.76
CONVERSION CO (%wt)	64.27	76.54	83.20
CONVERSION TOTALE (%wt)	63.72	75.66	82.00
PRODUITS (%wt)			
HC TOTAL / INPUT	10.79	15.29	17.65
HC (LIQ) / INPUT	2.62	5.41	6.08
HC (GAZ) / INPUT	8.17	9.87	11.57
EAU / INPUT	2.38	5.40	5.09
CO / INPUT	33.24	21.86	15.64
CO2 / INPUT	38.70	49.41	57.40
H2 / INPUT	3.03	2.48	2.36
BILAN MASSE (%wt)	88.14	94.45	98.14
SELECTIVITE:(C1-C4)/C5+	3.12	1.82	1.90
P O N A (%wt)			
P / HC (LIQ)	26.19	28.78	26.46
O / HC (LIQ)	30.75	30.75	31.80
N / HC (LIQ)	11.86	11.86	11.30
A / HC (LIQ)	29.20	29.20	28.44
C1/HC TOTAUX	26.55	23.93	25.19
C2/HC TOTAUX	11.93	10.36	11.16
C3/HC TOTAUX	10.22	8.52	8.45
C4/HC TOTAUX	19.70	15.75	14.90
C5+/HC TOTAUX	31.60	41.44	40.30

DISTILLATION SIMULEE
ASTM D2887

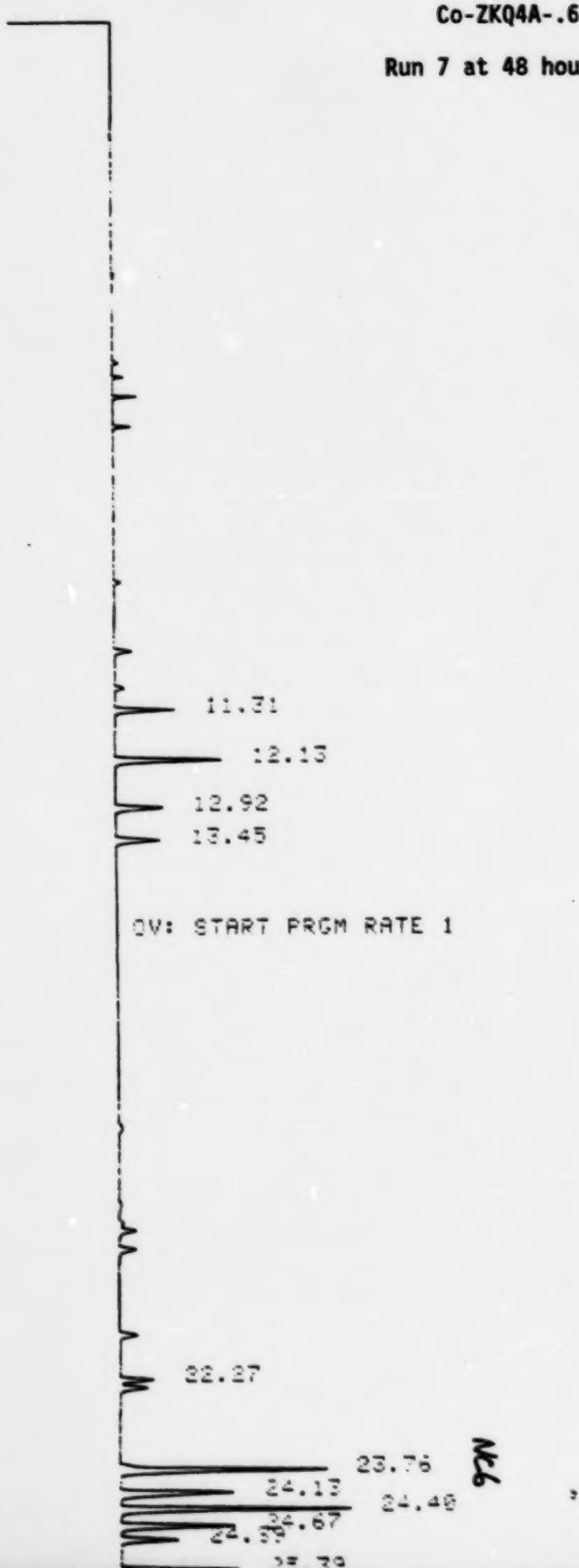
% OFF (C)				Diesel
IBP	30	25	25	124
10	90	90	88	198
20	109	110	109	222
30	120	121	121	242
50	138	142	142	278
70	158	163	163	311
80	169	178	178	329
90	184	199	199	351
FBP	288	316	311	405

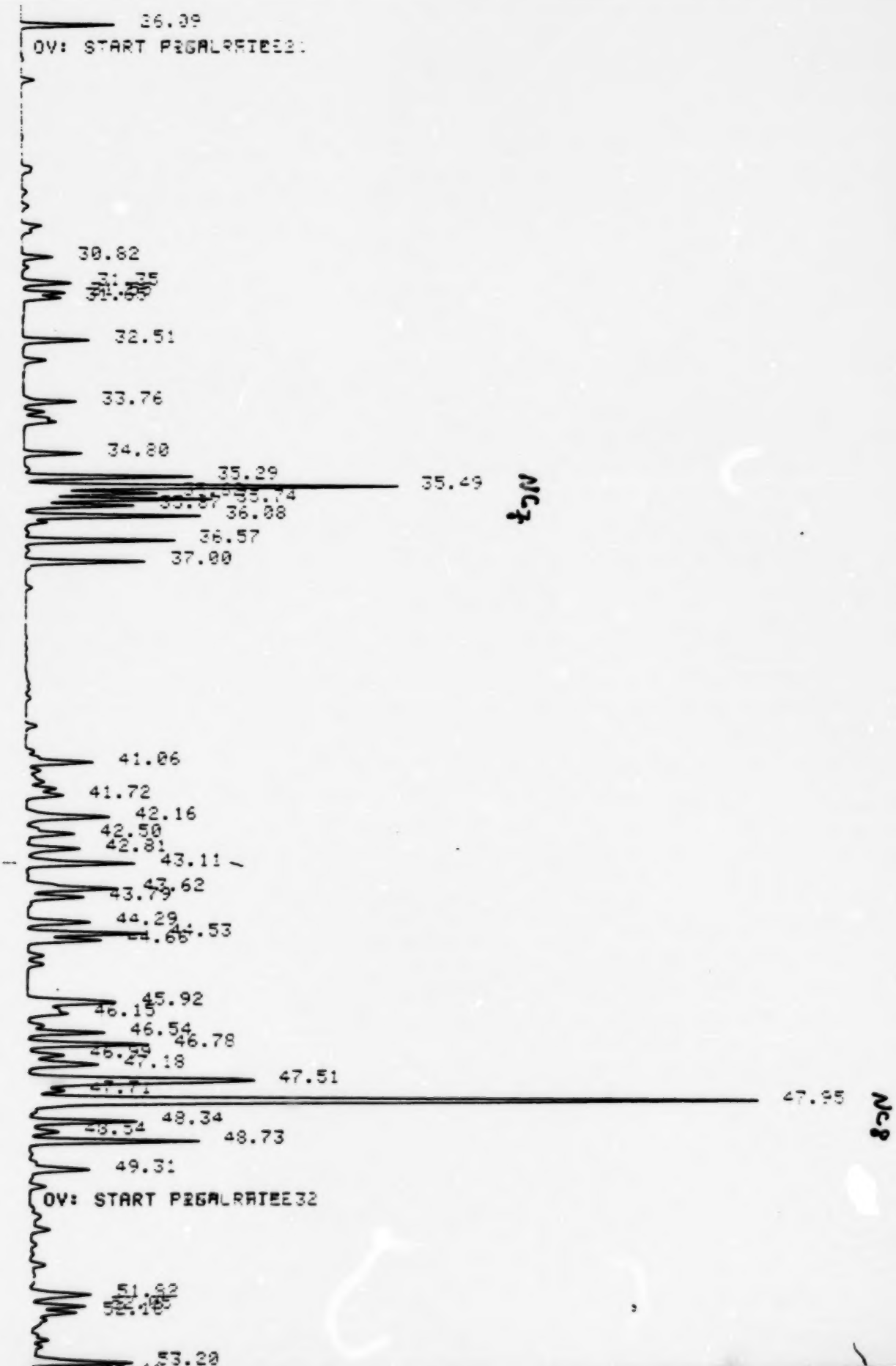
APPENDIX B

GAS CHROMATOGRAMS OF DISTILLATE FROM
A) CATALYST Co-ZKQ4A-.67Na(La)
RUN 7 AT 48 AND 336 HOURS-ON-STREAM
B) LONG DURATION TEST AT KINGSTON

Co-ZKQ4A-.67 Na(La)

Run 7 at 48 hours-on-stream

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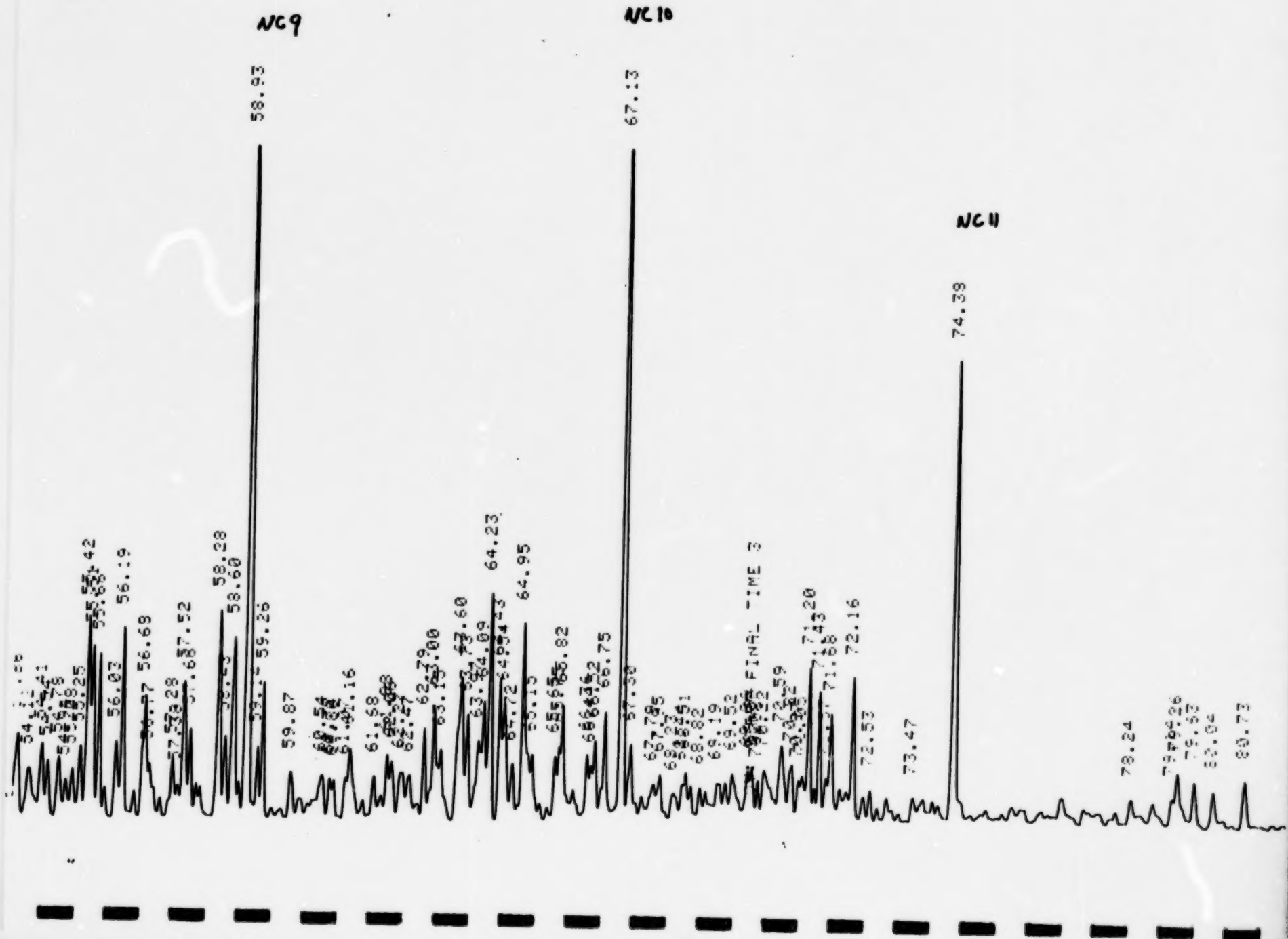
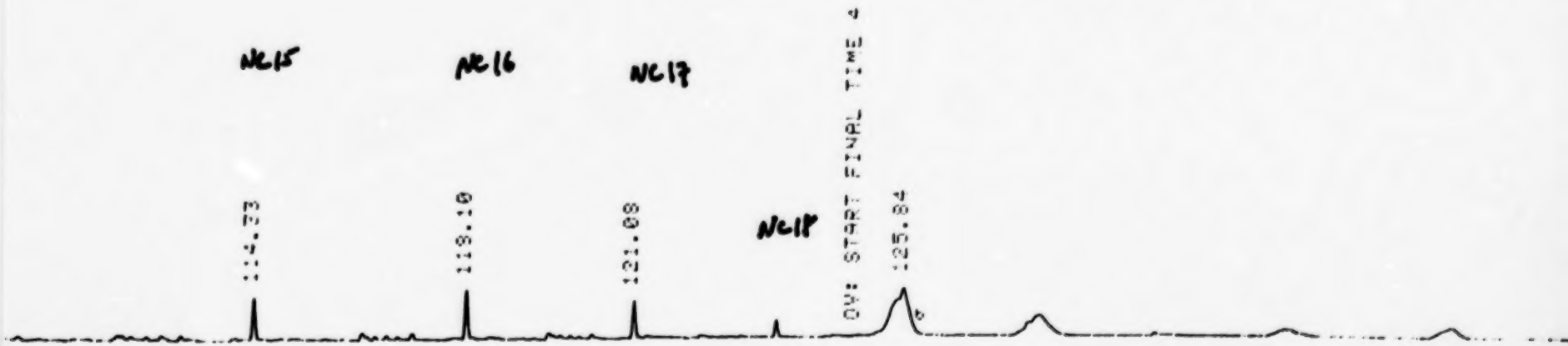
NC8


NC9
NC10
NC11
58.93
67.13
74.38
FINAL TIME 3

83.84
NC12
98.24
NC13
OV: START PRGM RATE 4
109.03

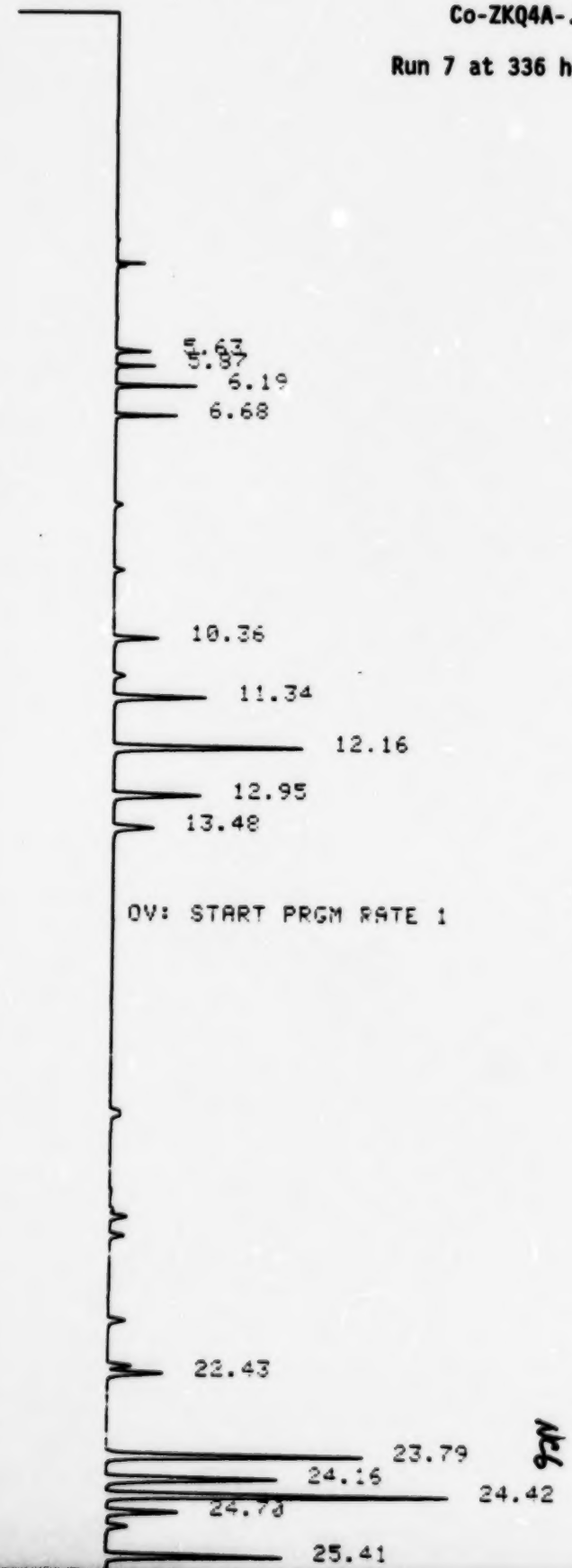

NC15
NC16
NC17
NC18
114.73
118.10
121.68
125.84
DW: START FINAL TIME 4

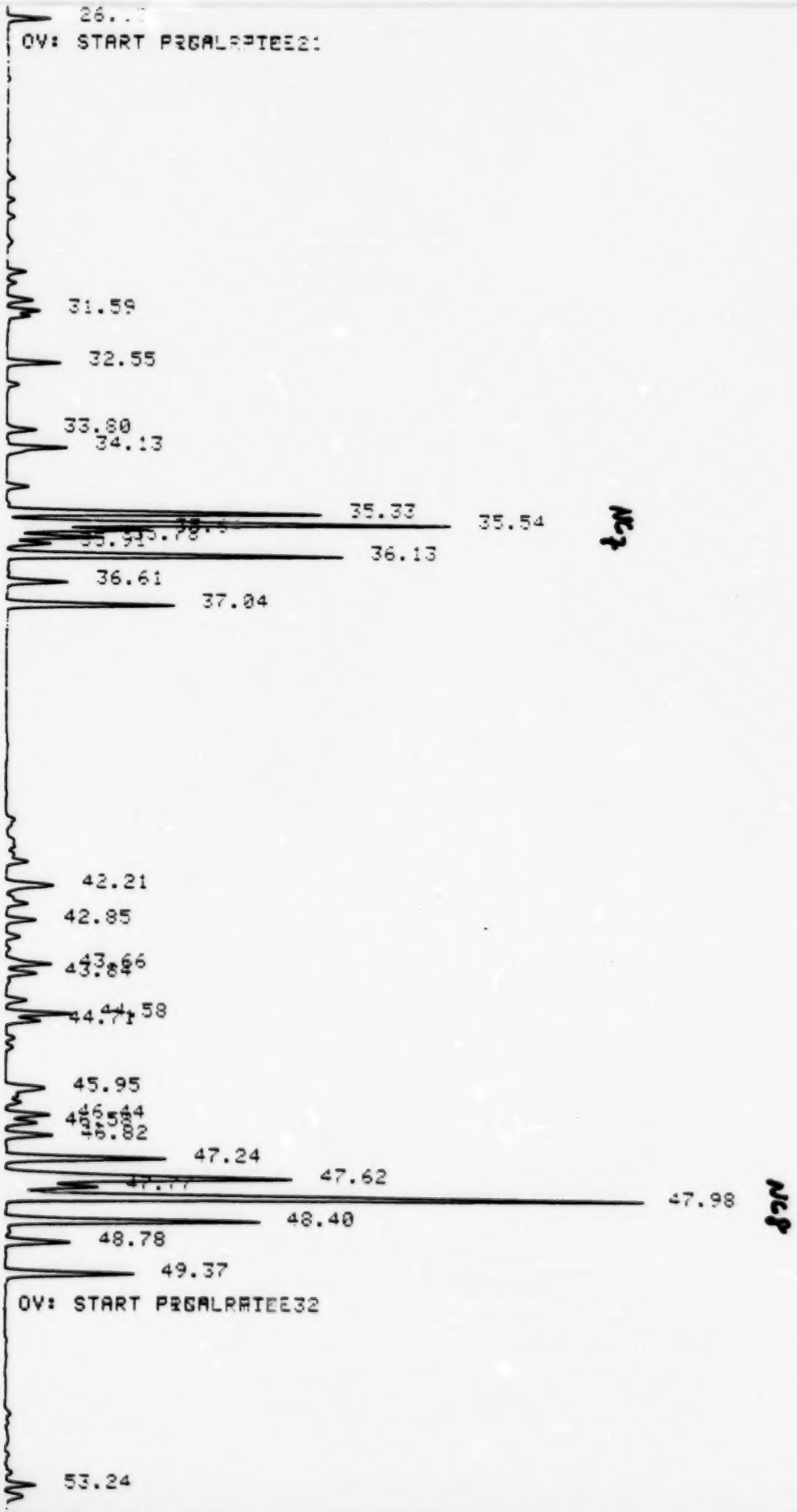
```
RT: STOP RUN
```

OVEN TEMP NOT READY

Co-ZKQ4A-.67 Na(La)

Run 7 at 336 hours-on-stream




OV: START PRGALRPIEE2:
31.59
32.55
33.80
34.13
35.33
35.54
36.13
36.61
37.04
42.21
42.85
44.71
45.95
47.24
47.62
47.98
48.40
48.78
49.37
OV: START PRGALRMIEE32
53.24

54.59
56.22
56.71
58.96
NC9
62.29
63.60
64.98
66.49
67.16
NC10
67.92
69.58
OV: START FINAL TIME 3
70.65
72.20
74.43
NC11
78.33
79.32
80.11
80.31

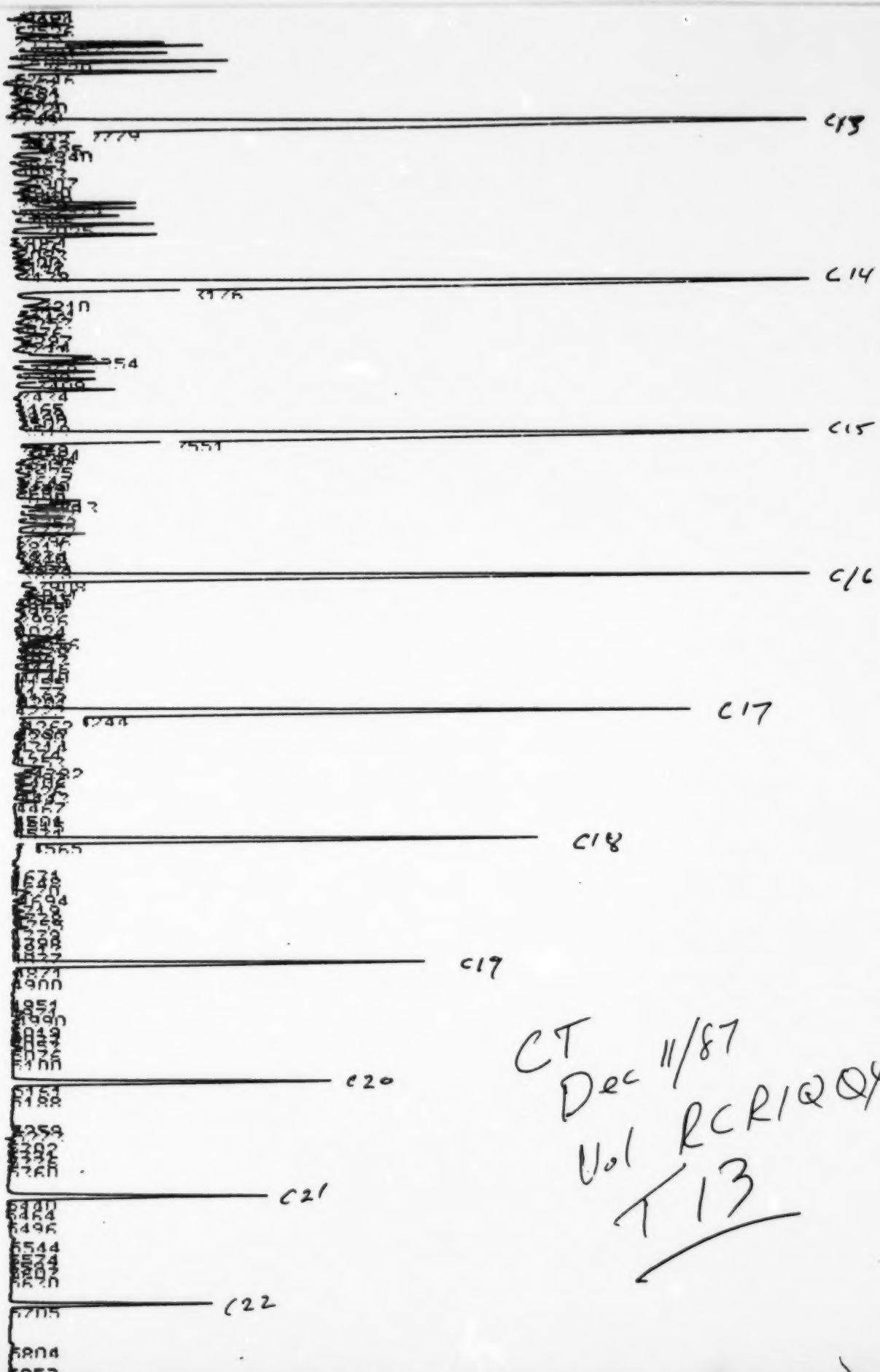
83.95
NC12
98.48
NC13
OV: START PRGM RATE 4
105.35
106.62
106.05
106.48
107.03

112.48
113.09
114.40
116.30
115.72
117.18
118.16
119.59
119.97
120.36
121.13
122.29
122.65
122.99
123.65
124.63
W: START FINAL TIME 4
125.90
126.82
128.10
128.99
130.35
132.81
135.62

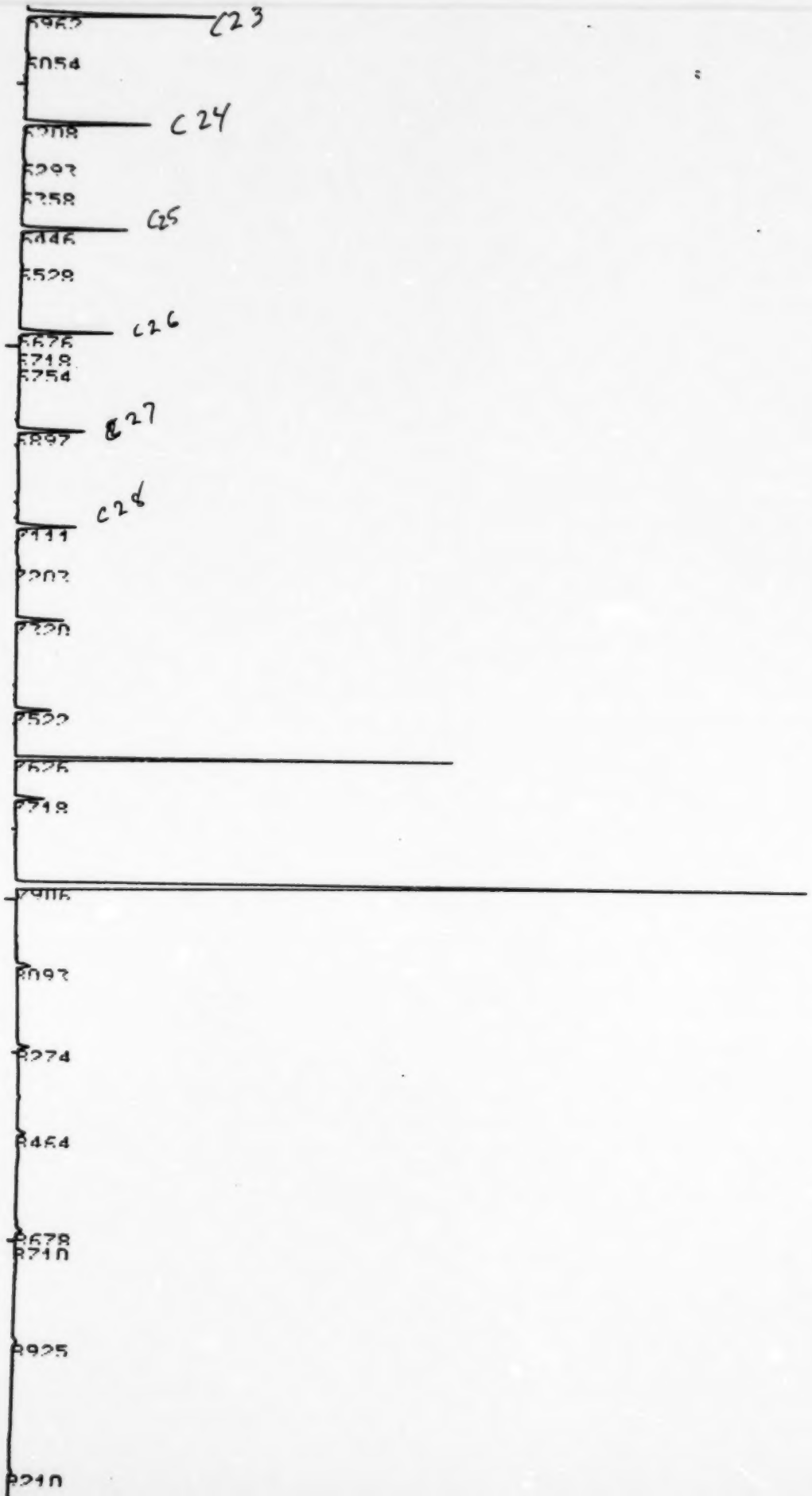
138.94
142.93
147.80
RT: STOP RUN

Co-ZKQ4A-.67 Na(La)

long duration test



CT
Dec 11/87
Vol RCR1Q04
T13


C23
5054
C24
5297
5358
C25
5529
C26
5718
5754
C27
C28
7444
7525
7718
8097
8274
8464
8678
8710
8925
9210

APPENDIX C

REPORT FROM PROFESSOR B.W. WOJCIECHOWSKI

DEPARTMENT OF CHEMICAL ENGINEERING
DUPUIS HALL

Queen's University
Kingston, Canada
K7L 3N6

March 24, 1988

Mr. Kee Leen
CRIQ-NRC
Montreal Road
Building M-55, Room 64
Ottawa, Ontario K1A 0R6

Dear Kee,

As you know, we have had trouble with our computers for interpreting the data on your runs on the "diesel" catalyst. I can only give you, therefore, some qualitative results, no mass balances.

You have already received the pooled liquids from the six weeks of running and have no doubt drawn your own conclusions regarding product characteristics; however, I will go on record to say the product was indeed much more in the diesel range than in the gasoline range. Most of the product lay in the range C_{10}-C_{20} so that some heavy gasoline (C_{10}-C_{12}) was present and most of the aromatics were in that range. You can see this in the total ion chromatogram (Fig. 1), where various product peaks are identified to give you an idea of carbon number in each vicinity. Figure 2 shows m/e of 91 which is a characteristic of aromatics. You will note that there is very little of the stuff and most falls below C_{12}. Thus, the diesel made is largely composed of straight chains and should have good cetane and low smoke.

Figure 3 shows some detail in the region 3700-4600 scans. On Figure 1, this region shows a lot of smaller peaks and these are identified in Figure 3. The second highest peak groups are clearly monomethyl alkanes. These groups repeat at each carbon number and constitute a typical "classical" Fischer-Tropsch product pattern. Their total yield at each carbon number is less than 5%. The smaller peaks on Figure 3 are also mostly polymethyl alkanes leaving very little to be assigned to aromatics.

over.../

Subsequent mass spectrograms scan for m/e's characteristic of olefins, e.g. 98 → C_7H_{16}. It seems that olefins are not a major product in this synthesis. All the high peaks in the olefins scans correspond to those in the alkane scans and are merely fragments of alkanes with two hydrogens missing.

In summary, the catalyst makes good diesel.

We also carried out simulated distillations on the liquid product. This showed a split of about 6% gasoline and about 75% diesel on an average. There were some variability in this result which was due to the small samples collected each day. However, towards the end of the run, the samples were in this range for the last ten days or so.

As per your request, the sample was run at 1:1 H_2/CO ratio, SV of 300 hr^{-1}, pressure 150 psi and 300°C for most of the time. Conversion was poor, we estimate some 20-30% but because of the computer failure, cannot give a number. The low conversion may be due to improper packing of the reactor and resultant bypassing of the bed. If this did occur, the conversion can be expected to be better in practice.

A four day run at 2:1 H_2/CO gave even less conversion and no liquid product to speak of. The gases made in that case, as in the 1:1 case, were mostly saturates with olefins being very low at C_2, about 30% at C_3, down to 25% at C_4 and on down until at C_6, C_7 where there are practically no olefins. This may be a desirable situation in that C_3 and C_4 olefins are most desirable for gasoline synthesis or even for oligomerization into the diesel range.

The most recent catalyst is clearly a diesel making catalyst and contrasts sharply in its product spectrum with the ZMQ-IB gasoline-making catalyst tested previously in our laboratories.

over.../

I trust this will be of assistance in your fine work on "tailoring" catalysts to produce diesel or gasoline selectively.

Yours sincerely,

B.W. Wojciechowski
Professor
Chemical Engineering Dept.

P.S. Please direct payment to Queen's University account no. 377-235-08 and send the check to me.

BWW/vmd

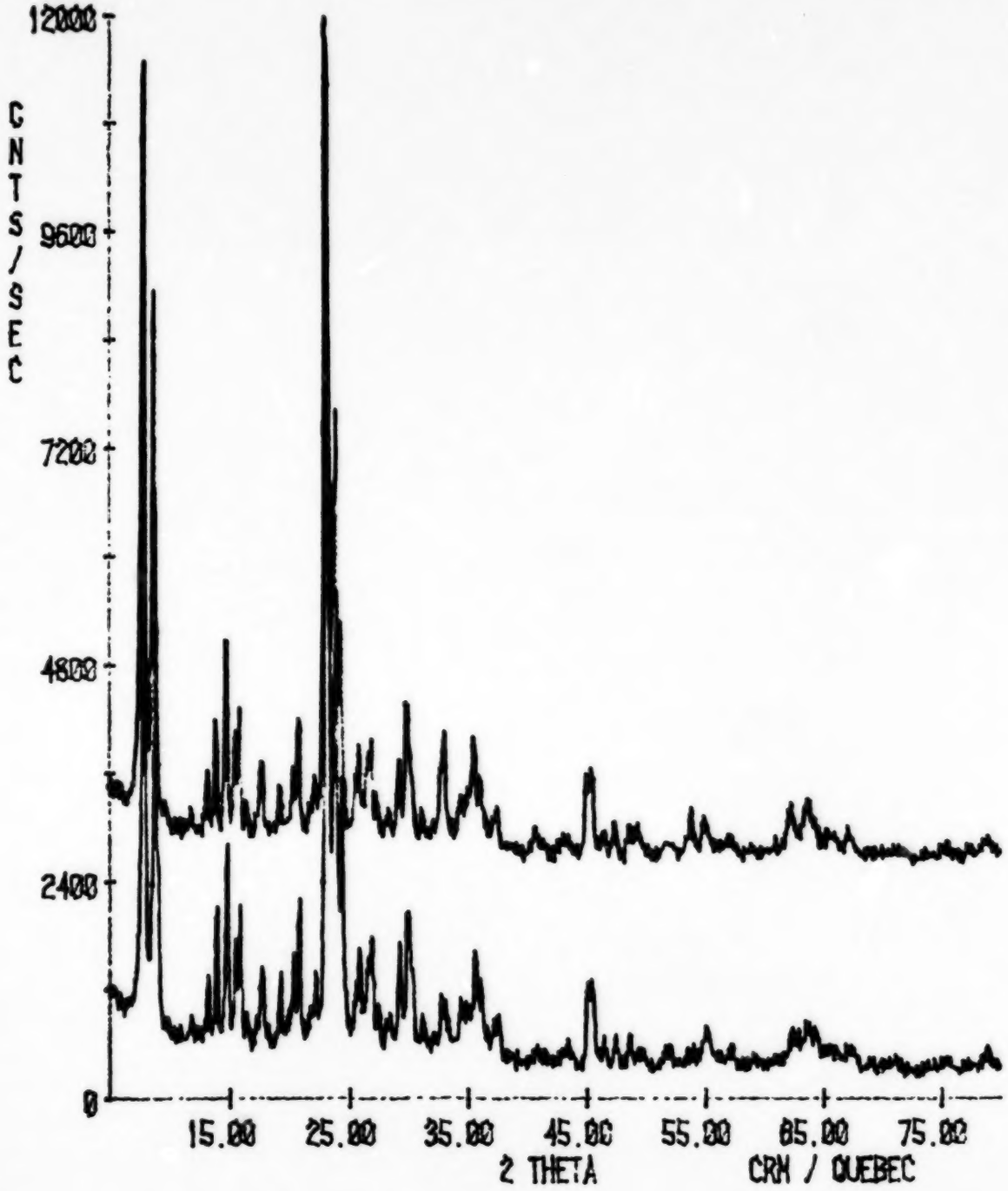
Encls. GC/MS analyses

APPENDIX D

X-RAY POWDER DIFFRACTION PATTERN

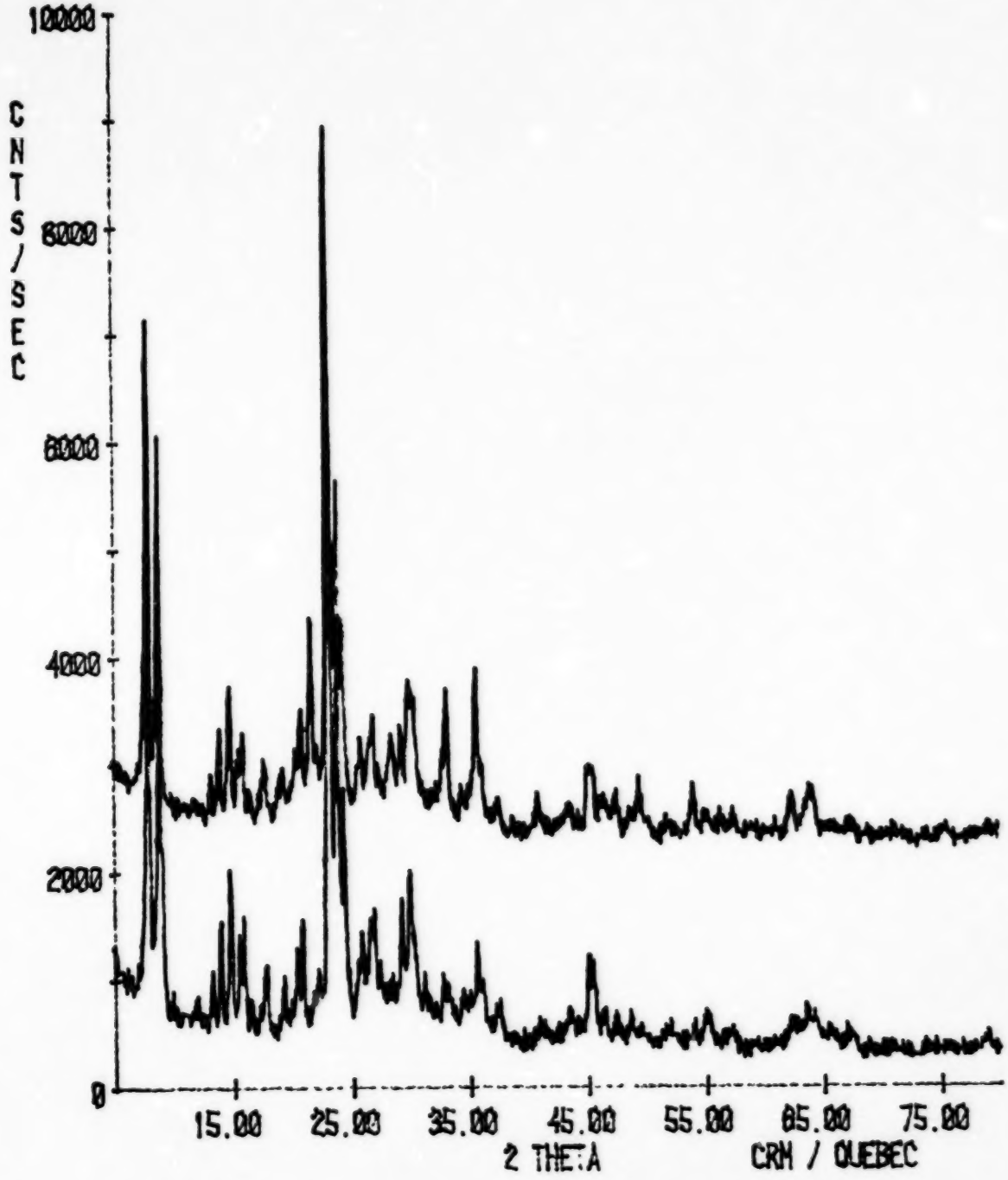
A) ZKQIB4A
B) Co-ZKQIB4A-0.67Na (La)

CRIQ



ZKQIB4A: Upper: heated at 950°C
Lower: calcined at 500°C

Z02187 10/20/87 DIF S=0.05 T= 0.4 CRIQ #2 CO.5NAZKQ
Z02171 10/20/87 DIF S=0.05 T= 0.4 CRIQ #2 RESIDU THERMOBALANCE 950C



Co-ZKQIB4A-0.67Na(La)

Upper: heated at 950°C
Lower: calcined at 500°C